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CONTROL OF SULFUR DIOXIDE EMISSIONS FROM COPPER SMELTERS. VOLUME II. HYDROGEN SULFIDE PRODUCTION FROM COPPER CONCENTRATES

BATTELLE-PACIFIC NORTHWEST LABORATORIES

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16. ABSTRACT The report gives results of a laboratory study of the control of SO2 emissions from copper smelters by H2S production from copper concentrates. Digestion of neutral roasted pyritic copper concentrates with HCl was studied as a means of producing sufficient H2S for reaction with the SO2 from converter gas to produce elemental sulfur and then minimize SO2 emissions from copper smelters. In this step the copper sulfides are maintained in insoluble form. A large fraction of the iron was shown to be solubilized with equivalent production of concentrated H2S at relatively low temperatures. In such a process a pure form of iron oxide would be produced as a by-product during acid regeneration. In the integrated scheme, digestion would likely be the only step which is not a state-of-the-art process. An economical overall process appears probable to yield elemental sulfur and also pure iron oxide as useful by-products. Costly reverberatory furnaces would be eliminated. Needs for slag forming minerals would be greatly reduced. With efficient utilization of excess pyrite, increased recovery of copper and precious metals from the ore body should also be realized. Further laboratory studies are recommended in preparation for pilot plant investigations.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Hydrochloric Acid	Air Pollution Control	13B
Sulfur Dioxide		Stationary Sources	07B
Copper Ores		Pyritic Copper	
Smelters			11F
Smelting			13H
Hydrogen Sulfide			

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CONTROL OF SULFUR DIOXIDE EMISSIONS FROM COPPER SMELTERS: VOLUME II - HYDROGEN SULFIDE PRODUCTION FROM COPPER CONCENTRATES

ABSTRACT

A laboratory investigation has been made of a modified copper smelting process which provides a solution to the sulfur dioxide air pollution problem and produces blister copper, elemental sulfur, and iron oxide without loss of the precious metals. Preliminary economic evaluation of the process appears favorable with good prospects for further improvements when compared with conventional processes provided with equivalent air pollution abatement capabilities.

The process would involve (1) neutral roasting of pyritic copper concentrates to convert the contained iron into an acid-soluble form with evolution of some elemental sulfur in this step, (2) hydrochloric acid leaching of the roasted concentrate to dissolve the iron with simultaneous hydrogen sulfide generation and production of an enriched copper sulfide residue, (3) converting the copper sulfide residue to blister copper by conventional means, (4) reducing the sulfur dioxide formed in the converting step to elemental sulfur with hydrogen sulfide from the leaching step, and (5) processing the iron chloride leach solution to regenerate hydrochloric acid and to yield a marketable iron oxide. Step 1 (for pyrite conversion), as well as steps 3, 4 and 5, are regarded as present industrial state-of-the-art. Step 2, based on the results from the principal focus of this laboratory study, would involve relatively straightforward chemical engineering development for scale-up to pilot-plant scale to demonstrate feasibility.

Principal advantages of the process include: (1) hydrogen sulfide production without requiring the utilization of a specific chemical reductant such as costly natural gas or coke; (2) elimination of the costly investment and operations of reverberatory furnaces with their accompanying high fuel demand, dilute sulfur dioxide flue gas releases and concurrent

formation of massive amounts of high-temperature solid wastes; (3) major reductions in the requirements for slag-forming minerals; and (4) probable increased overall recovery of copper and precious metals from a specific ore body.

CONTROL OF SULFUR DIOXIDE EMISSIONS FROM COPPER SMELTERS:
VOLUME II - HYDROGEN SULFIDE PRODUCTION FROM COPPER CONCENTRATES

SUMMARY

As a result of the laboratory work done under this project, it has been determined that: (1) by neutral roasting of pyritic copper concentrates at 800°C or higher a large fraction of the iron in such concentrates is converted to an acid-soluble sulfide form; (2) by dissolution of the solubilized iron in 4-5N hydrochloric acid at 80-85°C large quantities of concentrated hydrogen sulfide can be readily obtained; (3) an enriched copper sulfide still containing the precious metals is readily separated from the acidic iron chloride solution; and (4) the small amounts of copper which are also dissolved can be readily recovered by treatment of the cooled acidic-iron chloride solution with hydrogen sulfide. This treatment also assures the retention of the precious metals, principally silver, with the copper sulfide residues.

The regeneration and recovery of the hydrochloric acid from the ferrous chloride solution as produced above is regarded as a present state-of-the-art commercial process applied on a substantial and increasing scale in the steel pickling industry.

The conversion of the moderately-concentrated sulfur dioxide evolved from conventional copper smelter converters to elemental sulfur by reaction with the hydrogen sulfide produced as indicated above is also regarded as a present state-of-the-art process, the so-called Claus process. However, an alternative means utilizing the U.S. Bureau of Mines Citrate process, which is in a fairly advanced state of development, may also be employed for elemental sulfur production.

The production of blister copper from the enriched copper sulfide concentrate obtainable by the above treatment is regarded as a present state-of-the-art process which can be accommodated in copper smelter converters of the existing design.

Thus the technical, or at least the chemical, feasibility of the processes necessary for the recovery of elemental sulfur in high yield and quality from copper smelter flue gases without need for a specific and increasingly more costly chemical reductant such as natural gas or coke has been demonstrated on the laboratory scale. This is regarded as the positive answer to the principal original objective of this investigation.

In reviewing the composition of representative pyritic copper concentrates and the results of this project, essentially all such concentrates are and can be expected to be deficient in pyrite. However, it is also understood that all but a very few copper sulfide ore bodies are characterized by having an excess of pyrite present. Suitable copper sulfide-iron sulfide concentrations for matte production are almost universally obtained by depressing the flotation of the excess pyrite and thus rejecting it to the tailings. It is thus accepted that sufficient pyrite for the conduct of the proposed process already exists in almost all copper sulfide ore bodies and that by moderate, tolerable and probably desirable changes in flotation process control, the required amounts of pyrite could be concurrently or separately recovered without difficulty or significant economic penalty. For chemical reasons as developed in this laboratory study, separate recovery and processing of the required additional pyrite appears preferable.

The overall investment and operating costs as determined by a preliminary economic study of the proposed copper smelting process (through anode production) with a capacity of 300 tons of copper per day shows it to involve an investment of about $52,000,000 and an overall smelting cost for copper of about 12 cents per pound without credit for recovered elemental sulfur and iron oxide. Both of these resources are regarded as marketable and at values that are regarded as conservative under today's conditions (at $20 and $10 per short ton for sulfur and iron oxide, respectively) the overall smelting cost for copper drops to about 9 cents. Although a detailed estimate and comparison with a conventional smelter was not made, it is understood that such smelting costs (through anode copper production) are 7 to 8 cents per pound, but without equivalent sulfur emissions control. However, with such controls another 5 to 6 cents per pound would be added. It is felt that a detailed study of the proposed process could identify substantial economies which would reduce the overall production cost significantly.

The overall assessment of the chemical, technical and economic feasibility of the proposed process is definitely regarded as favorable at this stage.

Continued work at the bench-scale level to obtain data suitable for pilot plant design, particularly work involving the continuous rather than batch operation of the two principal processes of neutral roasting and acid dissolution, is recommended.

In view of the results of this study and the near and actual state-of-the-art technology which may be employed for the principal processing operations, it is concluded that the overall proposed process has favorable prospects for achieving an adequate and economically acceptable control (97%) of sulfur dioxide emissions for conventional smelting processes integrated with the proposed process.

INTRODUCTION

Although in the U.S. four copper producers* have announced plans for non-smelting type processes to augment normal production or for large pilot plant operations, a review of worldwide copper smelting practices involving about 100 major plants shows no trends to indicate a significant shift away from conventional roaster-reverberatory-converter type overall operations. Roasters, when required, are generally used to adjust the sulfur content of the charge to the reverberatory furnaces. Reverberatory furnaces are used to adjust the iron content and to produce molten matte (a fluid homogeneous mixture of iron and copper sulfides). Converters are used to produce blister copper from matte. Blister copper is a relatively impure metal containing some copper oxide, the precious metals and other impurities such as nickel and selenium. However, in order to meet the increasingly more stringent regulations on sulfur dioxide emissions, there is a very definite trend in the U.S. and elsewhere to initiate major changes in the smelting practices, the objective being mainly to assure the production of higher strength sulfur dioxide waste gases from which principally sulfuric acid can be produced most efficiently and thus realize a major reduction in sulfur dioxide emissions. In many cases this acid is finding use nearby in expanded leaching operations for low-grade oxidized copper ores. The changes in smelter practices do, however, involve major changes in smelter equipment such as for flash smelting and continuous converting. One plant in the U.S. (Tennessee Copper Co.) converts part of its waste gas to liquid sulfur dioxide. The American Smelting and Refining Co. plant at Tacoma, Washington, is about to begin very large-scale production of liquid sulfur dioxide from a portion of the concentrated converter gas that is not used for sulfuric acid manufacture. Although consideration is being given at some plants to convert concentrated gas to elemental sulfur or to dispose of excess sulfuric acid by conversion to waste gypsum, no plants are known to be operating such processes on a large scale today in the U.S. One new copper producer (Hecla Mining Co.) is to operate roasters to produce oxide copper and sulfuric acid for a leaching and electrowinning process.

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* Cyprus Mines: The Cymet Process
Duval Corp.: A Chloride Leach Process
Anaconda: A Low-Pressure Ammonia Leach Process
Hecla: A Roast-Leach-Electrowin Process

In general, the conversion of waste sulfur dioxide to elemental sulfur has been regarded as an ideal solution to the problem. Activity in this direction has generally been concerned with the chemical reduction of the sulfur dioxide utilizing natural gas or coke as the reductant. At some point in the chemistry of natural gas reduction, hydrogen sulfide is regarded as being formed, then the usual reaction between hydrogen sulfide and unconverted sulfur dioxide proceeds to form elemental sulfur. Thus hydrogen sulfide appears as a logical reagent for effective conversion of sulfur dioxide to elemental sulfur. Consideration of processes for hydrogen sulfide production without the use of a chemical reductant such as natural gas have not received much attention. However, this was the objective of the earlier efforts on this present project where H_2S production was accomplished by reaction of high-temperature water vapor with the residual iron sulfide obtained in an initial step of neutral roasting of the pyritic copper concentrate. This process was shown to be unfavorable because of unsatisfactory equilibrium conditions from which only very dilute (less than 1%) hydrogen sulfide gas was obtained. Accordingly, such production and effective conversion of the iron sulfide was achievable only by treatment with very large volumes of high-temperature water vapor. Preliminary economic studies showed this process to have unlikely prospects for economic viability.

An alternative process was subsequently scoped. In this process (1) neutral roasting would still be required (including in many cases provision of additional pyrite) followed by (2) acid treatment for hydrogen sulfide production, (3) acid regeneration and recovery, and (4) enriched copper sulfide recovery for delivery to conventional converters. The sulfur dioxide from the converting step would be (5) reacted with an adequate amount of hydrogen sulfide from the acid treatment step to produce elemental sulfur. This sulfur, together with that evolved from the neutral-roasting step, would comprise essentially all of the sulfur present in the original pyritic copper concentrates. Thereby overall production of elemental sulfur would be achieved by thermal means without the need for a specific chemical reductant. This present report covers the details of the laboratory efforts directed at assessing the chemical feasibility of such a process and its economic potential. The principal areas for study include: (1) the neutral-roasting step and (2) the acid-leaching or hydrogen-sulfide production step. Related matters concerned with feed, residue and gas composition were studied concurrently.

Most copper sulfide resources in the U.S. and throughout the world are associated with pyrite. For the recovery of concentrates from these ores flotation treatment is generally used. In this treatment excess pyrite which is generally present in substantial amounts is discarded along with the gangue. This is accomplished by simple chemical adjustments in the concentrator to preferentially depress the flotation of the iron sulfide (pyrite) and thus reject it from the circuit. Since in most cases additional iron sulfide is essential to the process to provide the required amounts of hydrogen sulfide, it is a requirement of the suggested process concept that sufficient pyrite be retained with the copper sulfide concentrates (or separately recovered) for subsequent use. This appears to be easy to accommodate in existing concentrators.

BACKGROUND

THE OVERALL CONCEPT

Although the individual steps of the proposed process concept comprise well-known and fairly well-understood chemistry and technology, the combination of these steps or processes to achieve the desired objective specifically in copper smelting appears not to have been explored. The patents by S. I. Levy(1,2) employ similar steps specifically to treat pyrite for recovery of iron, sulfur and other metals such as copper, lead and zinc. These patents disclose the combination of steps of neutral roasting, the recovery of sulfur from neutral roasting, hydrogen sulfide conversion to sulfur, hydrochloric acid treatment to preferentially dissolve iron and liberate hydrogen sulfide, the separation of a copper-rich residue, the regeneration of hydrochloric acid with iron oxide recovery and, in addition, the recovery of zinc and lead by separate electrolytic processes. The technology employed for iron and hydrochloric acid processing was different from more recent processes by involving crystallization of the chlorides as the primary means of separation from other metal chlorides which may be present in substantial amounts. The inventions do not include the further processing of insoluble copper residue or the utilization of hydrogen sulfide to react with any sulfur dioxide derived therefrom.

NEUTRAL ROASTING

The literature on the chemistry and technology of neutral roasting wherein pyrite is thermally decomposed to yield elemental sulfur and pyrrhotite is extensive and goes back many years; however, much of it is not of sufficient relevance to be useful in the present investigation. The most recent and useful compilation of background information has been reviewed in a report by Parsons and Ingraham.(3) The thermochemical mineralogy of the copper-iron-sulfur system has been intensively studied by many investigators.(5-25) This work has included consideration of the extremely complex and still imperfectly defined central portion of the system. Although simple chemical equations can be written to indicate the possible decomposition of the many copper-iron-sulfide compounds which may be present in practical pyritic copper concentrates to yield FeS, Cu_2S and sulfur, it is clear that such simplifications do not actually occur under conditions which are encountered in the present process concept.

As to the application of neutral roasting on a practical scale in recent years, perhaps the most noteworthy activity has been that of the Outokumpu Company in Finland relative to their flash smelting developments. This process has been indicated to utilize a neutral-roasting process on pyrite to produce elemental sulfur and molten iron sulfides (FeS).(26) This process has sufficient flexibility so that either neutral or almost any degree of oxidative roasting can be utilized. It is uncertain at present whether or not elemental sulfur production via neutral roasting is actually continuing today.

Kunda and Mehta and coworkers(27,28) have disclosed the details of a proposed very large-scale process for pyrite neutral roasting in Canada. These references are most useful for their engineering and economic details. Watkinson and Germain(29) of Noranda, also in Canada, have reported useful laboratory data on neutral roasting of pyrite intended for large-scale applications. No references to work specifically related to practical copper concentrate neutral roasting were uncovered although Tkachenko, et al., and Isakova, et al.,(30-32) reported on studies of the thermal decomposition of pyrite, chalcopyrite and bornite.

Although specific references to the neutral roasting of pyritic copper concentrates were not uncovered, the related work including actual large-scale applications to pyrite alone, which is a significant fraction of the neutral roasting processing as intended in the proposed process concept, leads to the conclusion that neutral roasting as proposed here is largely a present state-of-the-art technology.

LEACHING

The leaching of processed pyritic minerals with acids for preferential dissolution of iron comprises a very old concept. Parsons and Ingraham(3) have also extensively reviewed this. Their review indicates many concepts which recognize the relative insolubility of copper in such treatment processes. Van Weert, Ingraham and Thornhill and co-workers(33-35) recently reported on the leaching of nickeliferous pyrrhotites and matte with hydrochloric acid. In their discussion of this work, regeneration of hydrochloric acid from hydrated nickel chloride crystals was indicated as a commercial process. It was also mentioned that such technology was being extended to ferrous chloride. However, references to operating processes which utilize the chemistry of leaching were not uncovered. Leaching is, therefore, perhaps the major part of the proposed overall process which is definitely not present state-of-the-art technology. However, it appears to be a technology which is easy to develop to a practical scale and has been worked on by others on a laboratory scale at least.

ACID REGENERATION

Hydrochloric acid regeneration from corresponding acid-ferrous chloride solutions is also an old concept and recently, within the last ten years, has assumed considerable importance as the preferred and alternative means of providing a regenerative process for use in the steel pickling industry in the U.S. This process regenerates the pickling acid (hydrochloric acid) and produces concurrently iron oxide suitable for recycle in steel making. Reeve and Ingraham(4) have extensively reviewed this technology which derives mainly from European developed practices. Installations in the U.S. include the Ruthner-Dravo process and more recently the Lurgi process. The Turbulator Process, used in Europe and licensed in the U.S. by Haveg Industries, has apparently not yet been utilized in the U.S. The latter process is reported to be able to accommodate solutions as low as 0.5% and as high as 11% by weight in acid and up to 35% in dissolved ferrous chloride. This is support for the expectation that such processes have very wide ranges of flexibility for processing solutions of differing composition with essentially no practical limits. Acid regeneration and concurrent iron oxide production are clearly regarded as present state-of-the-art processes. The only problem here appears to be one of scale-up. Although pickle liquor processing as practiced is of substantial size, mainstream ferrous chloride decomposition and hydrochloric acid regeneration as contemplated in the proposed concept may be on a scale at least ten times as large as in a single pickle liquor regeneration plant. The selection of which existing process of those indicated above to use would be determined by ease in scale-up and ultimate detailed construction and operating costs.

CONVERTING

Converting of matte to blister copper is a well-established state-of-the-art process in essentially all sulfide copper smelters throughout the world. In the proposed process concept, a feed richer in copper sulfide would replace the usual matte composition. It is understood that such a change can be accommodated by adjustments in fuel and air or oxygen delivery to the converter to compensate for the absence of the large amounts of iron sulfide which are present in conventional mattes. The lowered iron in the feed will also result in substantial reductions in the amount of slag which will be produced by the converter. However, special (yet conventional) means would probably be needed to prepare this relatively small amount of slag for delivery back to the concentrator for flotation treatment for residual copper recovery.

SULFUR PRODUCTION

Sulfur production achieved by catalytically reacting sulfur dioxide and hydrogen sulfide is an old state-of-the-art process. Its principal application today is the process by which "sour gas" (natural gas containing hydrogen sulfide, normally as a major contaminant) is purified for widespread distribution and use. The reaction is also employed commercially in the petroleum refining industry as the means of cleaning the vent gases which may have intolerable hydrogen sulfide concentrations. In these processes (which are modifications of the so-called Claus process), the extracted hydrogen sulfide is partially burned to form the required ratio of hydrogen sulfide to sulfur dioxide. This mixture of gases is then reacted on a bauxite catalyst to yield elemental sulfur as either a gas, liquid or solid, depending on the temperature employed.

The Claus process, though effective and economical as normally operated, does not achieve complete reaction. The vent gas may require further treatment before release. Alternative processes have therefore been receiving increasing attention.

Another process which is fairly advanced in development is the U.S. Bureau of Mines Citrate Process.(36) It is primarily being considered as a means for removing sulfur dioxide from smelter flue gas (and has also been proposed for power plant flue gases) by absorption of the sulfur dioxide in buffered aqueous sodium sulfite-sodium citrate solutions followed by contacting with gaseous hydrogen sulfide (separately prepared) to yield elemental sulfur. The recovered sulfur is intended to be partially converted back to hydrogen sulfide by chemical reduction to provide the required amounts of hydrogen sulfide. This process is being installed by USBM on a demonstration scale using a sulfur dioxide-bearing flue gas stream from the lead smelter of the Bunker Hill Company at Kellogg, Idaho. This process is of special interest because of its expected capability for effective removal of sulfur dioxide from very dilute gas streams with accompanying high yields and effective conversion to elemental sulfur. In these features it may have significant advantages over the conventional Claus process for application in the proposed process concept. In any case, the high concentrations of sulfur dioxide expected from the converter gas stream and also the very high concentrations of hydrogen sulfide produced in the leaching step suggest that either a Claus process or a Citrate process may be utilized. If the Citrate process demonstrates substantially higher overall recoveries of sulfur from dilute flue gases, it may be the recommended choice. Its full demonstration, which is expected to be initiated this year, is awaited with interest.

PROCESS DESCRIPTION

The objective of the proposed process is to produce hydrogen sulfide by leaching neutral roasted copper concentrate containing iron sulfide with hydrochloric acid. The hydrogen sulfide is formed by the reaction of the acid with iron sulfide. Assuming the iron is present as FeS, the H_2S is formed according to the reaction:

$$FeS_{(s)} + 2HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_2S_{(g)}$$

The hydrogen sulfide can then be used to convert the sulfur dioxide in the smelter waste gas streams, particularly the converter gas, to elemental sulfur via the reaction

$$2H_2S_{(g)} + SO_{2(g)} \longrightarrow 3S_{(s)} + 2H_2O_{(g)}$$

Either a modified Claus process or the Bureau of Mines Citrate process(36) can be used to produce the elemental sulfur from the H_2S and SO_2.

The schematic flow diagram for the proposed process is presented in Figure 1. The principal operations in the process are as follows:

1. Run-of-mill flotation concentrate is dried at 150-200°C to remove water.
2. The dried concentrate is fired at 800-1000°C in a neutral or reducing atmosphere to remove the labile sulfur. The sulfur is condensed and collected. The roasting operation converts the bulk of the iron in the concentrate to a form that is soluble in hydrochloric acid.
3. The neutral roasted concentrate is leached in hydrochloric acid (4-5N) to dissolve the iron and convert an equivalent amount of the sulfur to hydrogen sulfide. In this step the copper sulfides are relatively insoluble.
4. The slurry from the leach tank is filtered and the solid residue washed with water.
5. The solids, containing the bulk of the copper and a small amount of iron, are sent to the converter for copper recovery.

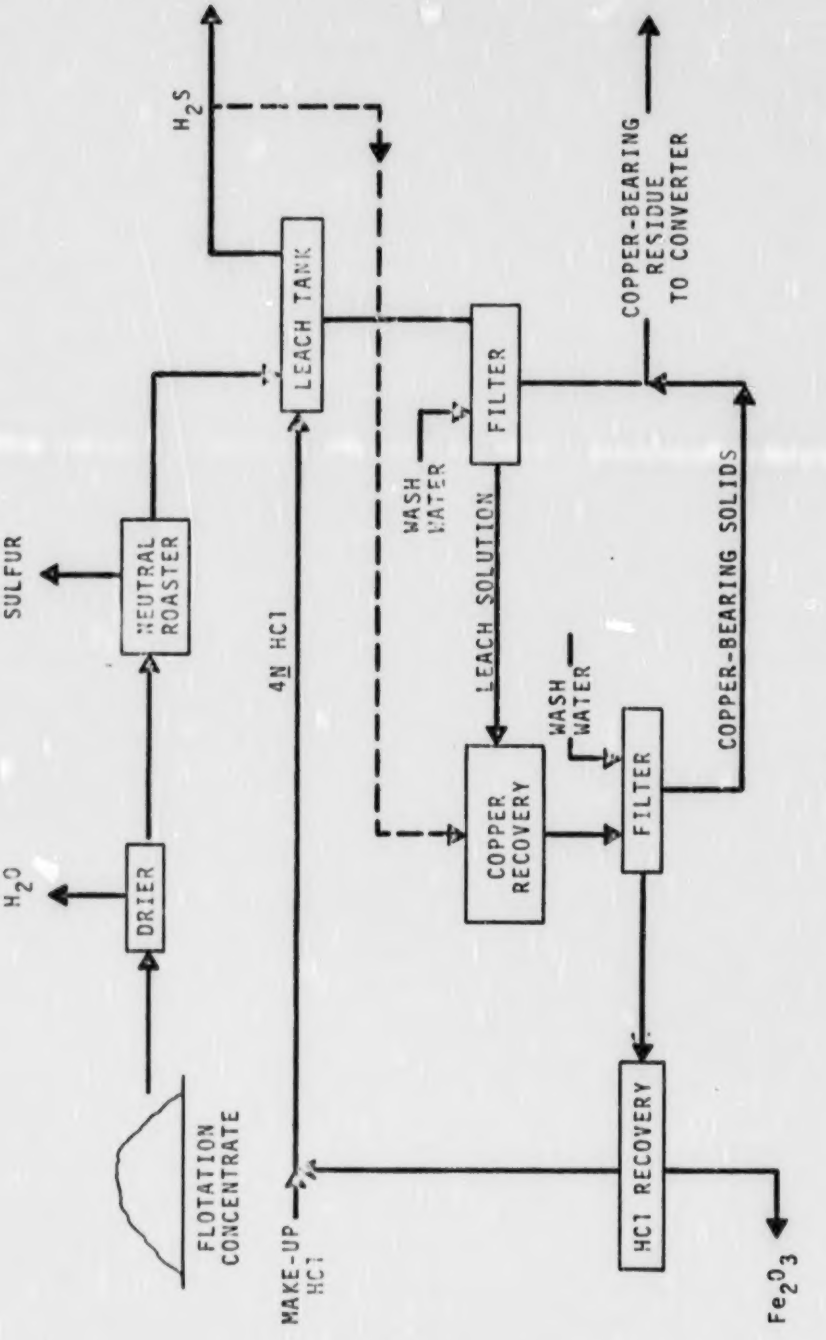
FLOTATION CONCENTRATE
DRIER
H_2O
NEUTRAL ROASTER
SULFUR
LEACH TANK
H_2S
4N HCl
MAKE-UP HCl
FILTER
WASH WATER
LEACH SOLUTION
COPPER RECOVERY
WASH WATER
FILTER
COPPER-BEARING SOLIDS
COPPER-BEARING RESIDUE TO CONVERTER
HCl RECOVERY
Fe_2O_3

FIGURE 1. Schematic Flow Diagram for Acid Leaching Copper Concentrates

6. The cooled leach solution, plus wash, which contains the bulk of the iron and small amounts of copper, is treated with a fraction of the H_2S. This precipitates the copper and some trace impurities, such as silver, as the sulfides. The precipitate is separated by filtration, washed, and sent to the converter for copper recovery.
7. The leach solution, which now consists of hydrochloric acid and iron chlorides (principally as ferrous chloride), is treated to convert the iron chlorides to ferric oxide and recover the hydrochloric acid for recycle. Commercially available processes used for treating hydrochloric acid pickle liquor can be used to process the leach solution.
8. Make-up hydrochloric acid is added to the process as necessary, to maintain the acid inventory.
9. In the converter the copper sulfide is reacted to form copper and SO_2.
10. The H_2S from the leaching step is collected and used to reduce the SO_2 from the converter to elemental sulfur.
11. The by-product sulfur and ferric oxide can be stockpiled or sold depending on market conditions.

In order for the process to achieve maximum utility it is necessary to produce enough H_2S in the leaching operation to react with all of the SO_2 produced in the copper smelter, primarily from the converting step. This means that about two-thirds of the sulfur in the neutral-roasted concentrate must be converted to H_2S. In actual practice more than two-thirds conversion must be obtained. There are two reasons for this: (1) some H_2S is needed to precipitate the dissolved copper and trace impurities in the leach solution; and (2) some SO_2 is formed in the neutral-roasting operation. It may be required that this SO_2 also be converted to elemental sulfur. In a typical commercial operation it would probably be necessary to convert about 70% of the sulfur in the neutral-roasted concentrate to H_2S in order to convert all of the SO_2 produced in the plant to elemental sulfur. For concentrates which are deficient in iron sulfide, additional amounts of iron sulfide (pyrite) would have to be provided. This is not regarded as a particularly critical problem because most sulfide copper ore bodies contain excess pyrite which is rejected by conventional control in the concentrator's flotation operations. Such excess pyrite could therefore be separately recovered or allowed to accumulate with the copper sulfide concentrate. It is probable that only a very few major sulfide ore bodies in the U.S. would be sufficiently deficient in pyrite to impair the likelihood of realizing a practical overall process.*

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* The White Pine, Michigan, operation of the Copper Range Co. is the typical example.

EXPERIMENTAL PROGRAM

The principal operations in the proposed process were demonstrated on a laboratory scale using glass and Vycor reactors. To simplify the experimental procedures the operations were carried in batch reactors rather than continuously.

COPPER CONCENTRATES STUDIED

In order for the proposed process to be applicable to a smelter operation, enough H_2S must be formed in the leaching reaction to combine with all of the SO_2 generated in other parts of the smelter (2 moles of H_2S required per mole of SO_2). The composition of the neutral-roasted concentrate can have a significant effect on the leaching reaction and on the H_2S formed. To evaluate the effect of composition, seven different copper concentrates, as well as pyrite, were studied in this program. The concentrates were obtained from various domestic copper producers as typical run-of-mill flotation concentrates. The chemical and mineralogical compositions of the concentrates studied are given in Table I. (The mineralogical compositions are those reported by the suppliers of the concentrates.) Three of the concentrates (Morenci, Pima, and Anaconda) were considered to be typical of the general types of copper concentrates produced in the United States and were studied in considerable detail. The Morenci concentrate was obtained from the Phelps Dodge Corp. and is principally a mixture of chalcocite and pyrite. The Pima concentrate was also obtained from the Phelps Dodge Corp. and is a mixture of chalcopyrite and pyrite. The Anaconda concentrate was obtained from the Anaconda Company and is a complex mixture of iron and copper sulfides as well as zinc, arsenic and antimony sulfides.

All of the concentrates contain varying levels of minor constituents which can affect their use in the proposed process. These include those materials which can affect the safety aspects of the process such as arsenic, antimony, mercury, etc., and the precious metals, gold and silver,

TABLE I. Composition of Concentrates Evaluated (Chemical Composition is in Weight Percent)

Element	Morenci	Pima	Anaconda	Tyrone	Lavender Pit	Battle Mountain	San Manuel	Hecla
Cu	20.82	27.14	26.93	20.31	12.65	24.50	29.58	
Fe	27.3	27.3	19.4	30.1	32.0	25.0	27.28	36.96
S	36.2	29.6	34.7	40.0	39.7	31.3	29.49	44.23
Insol.	9.12	10.16	6.64	6.48	8.88	13.12		
As	0.06	0.06	1.86	0.39	0.36	0.06		
Sb	0.025	0.025	0.037	0.05	0.03	0.063		
Zn	1.5	0.30	6.2	0.3	1.8	0.70		
Pb	0.04	0.04	0.05	0.04	0.20	0.03		
Mo	0.03	0.02	0.05	0.085	0.025	0.018		
Bi	0.008	0.016	0.03	0.012	0.024	0.020		
Cd	0.001	0.002	0.12	0.001	0.004	0.003		
Se	0.032	0.038	0.029	0.028	0.036	0.051		
Te	0.0068	0.0042	0.025	0.0058	0.011	0.0064		
Hg	0.028	0.028	0.024	0.031	0.024	0.038		
Ag*	1.82	2.8	10.42	1.54	1.94	10.79		
Au*	0.02	0.01	0.07	0.01	0.07	0.31		
	Chalcocite plus pyrite	Chalcopyrite plus pyrite	Complex Fe, Cu, As, Zn, Sb sulfides	Chalcocite plus pyrite	Complex Fe, Cu sulfides	Chalcocite, chalcopyrite, and pyrite	Chalcopyrite	Pyrite

* In troy ounces per ton

which must be recovered for their economic value. Therefore, it is necessary to know the fate of the minor constituents as the concentrates are processed.

Pima and San Manuel materials are typical of chalcopyrite concentrates. Morenci and Tyrone materials are typical of chalcocite concentrates. Anaconda and Lavender Pit materials are typical of complex sulfides characteristically high in zinc and arsenic. Battle Mt. and Anaconda concentrates are characteristically high in precious metals, gold and silver.

If one ignores the minor constituents, the concentrates have the following compositions:

Morenci	$Fe_{0.87}Cu_{0.58}S_2$	$(M_{0.73}S)$
Pima	$Fe_{1.06}Cu_{0.92}S_s$	$(M_{0.99}S)$
Anaconda	$Fe_{0.64}Cu_{0.78}S_2$	$(M_{0.72}S)$
Tyrone*	$Fe_{0.86}Cu_{0.51}S_2$	$(M_{0.69}S)$
Lavender Pit*	$Fe_{0.93}Cu_{0.32}S_2$	$(M_{0.63}S)$
Battle Mt.**	$Fe_{0.99}Cu_{0.85}S_2$	$(M_{0.92}S)$
San Manuel***	$Fe_{1.06}Cu_{1.01}S_2$	$(M_{1.04}S)$
Hecla****	$FeS_{2.09}$	

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* Also obtained from Phelps Dodge Corporation representative of their Tyrone, New Mexico, and Bisbee, Arizona, operations.

** Obtained from the Duval Corporation's Nevada operation.

*** Obtained from Newmont Mining Company's Magma Copper, Arizona, operations.

**** Pyrite concentrate representative of material from Utah, obtained from Hecla Mining Co.

NEUTRAL ROASTING OF CONCENTRATES

The neutral roasting of the various concentrates was carried out in an atmosphere of purified argon or helium, or under a vacuum (<100 microns absolute pressure). The concentrates were roasted at temperatures from 800 to 1020°C. A Vycor reactor was used to contain the concentrates at roasting temperatures up to 900°C; alumina was used for temperatures above 900°C. The general procedure used for neutral roasting the concentrates was as follows.

> A weighed amount of previously dried concentrate was placed in a horizontal Vycor reactor tube; the tube was purged with argon or helium. The reactor was heated in a tube furnace to the desired temperature and maintained at temperature for 6-24 hours. The reactor was then cooled to room temperature. The inert gas flow was maintained throughout the cycle. After cooling, the neutral-roasted concentrate was removed from the tube and ball-milled for one hour in a porcelain mill using alundum balls. The milled concentrate was screened through a 70-mesh screen and stored in a sealed glass jar. Oversize material was crushed and milled again.

When the neutral roasting was carried out in an alumina crucible, the procedure was modified as follows.

> A weighed amount of concentrate was placed in an impervious alumina crucible and the crucible was placed in a closed-end Vycor tube. The tube was placed in a pot furnace and purged with argon. The concentrate was then roasted in the manner described above.

When the roasting was carried out in a vacuum, a two-stage vacuum pump was used to maintain the vacuum. Two traps were placed between the reactor and the pump to prevent SO_2 and sulfur from entering the pump.

The bulk of the concentrates were roasted at 800°C under argon in one-kilogram batches. In the case of the Morenci, Pima, and Anaconda concentrates, several one-kilogram batches of each were neutral-roasted at 800°C. The various one-kilogram batches of each neutral-roasted product were combined and blended by ball milling for one hour. The composite blend of each concentrate was used for the bulk of the leaching studies.

Smaller batches of each of the three concentrates were neutral-roasted at temperatures above 800°C to determine the effect of temperature on the product and on the leaching reaction. At the maximum roasting temperature (∿1000°C) the three concentrates were partially melted.

ACID LEACHING OF NEUTRAL-ROASTED CONCENTRATES

Leaching of the neutral-roasted concentrates in hydrochloric acid was carried out in the laboratory employing equipment as illustrated in Figure 2. The reaction vessel is a one-liter three-necked flask. The procedure used in the leach tests was as follows.

1. The reaction flask was placed in a thermostatically controlled water bath.
2. The required volume of hydrochloric acid was added to the reaction flask.
3. The water in the bath was heated to the required temperature using a cartridge heater and thermoregulator. The temperature of the hydrochloric acid was monitored with a thermometer. The bath temperature and acid temperature, at equilibrium, never varied by more than 1°C.
4. Water in the bath and acid in the reaction flask were stirred using magnetic stirring bars and a stirring hot plate.
5. While the acid was being heated the reactor was purged with argon. Off-gas from the reactor passed through a water-cooled condenser and two traps. The bulk of the water in the off-gas was condensed in the condenser and returned to the reaction vessel. The first trap contained a dilute (∿0.5$\underline{N}$) hydrochloric acid solution and served to collect any hydrogen chloride in the off-gas. The second trap contained a known volume (usually 1 liter) of 1.5$\underline{N}$ sodium hydroxide and was used to absorb the H_2S in the off-gas.

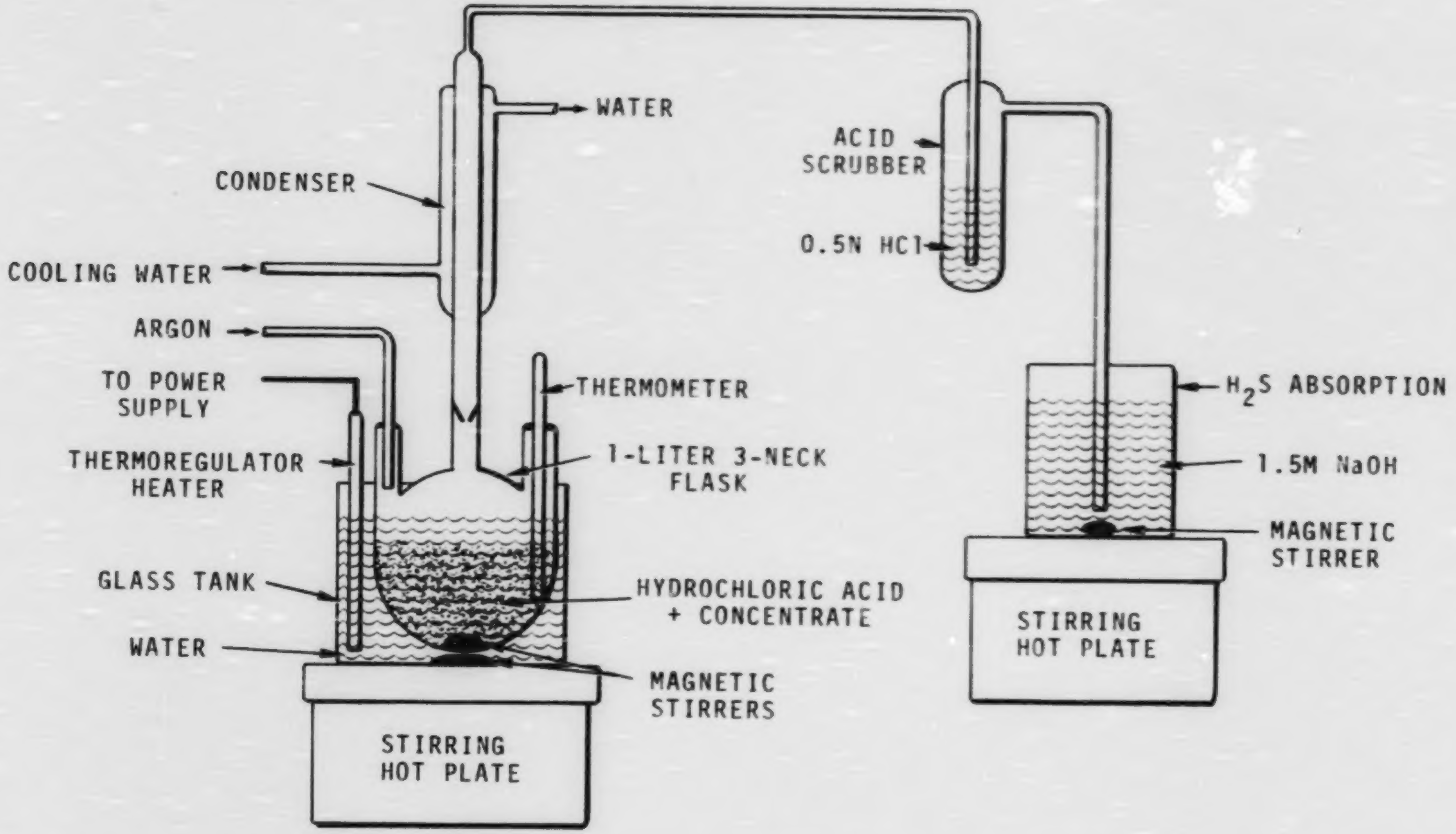
WATER
CONDENSER
COOLING WATER
ARGON
TO POWER SUPPLY
THERMOREGULATOR HEATER
GLASS TANK
WATER
THERMOMETER
1-LITER 3-NECK FLASK
HYDROCHLORIC ACID + CONCENTRATE
MAGNETIC STIRRERS
STIRRING HOT PLATE
ACID SCRUBBER
0.5N HCl
H_2S ABSORPTION
1.5M NaOH
MAGNETIC STIRRER
STIRRING HOT PLATE

FIGURE 2. Equipment for Leaching Neutral-Roasted Concentrates in Hydrochloric Acid

6. When the acid reached the desired temperature the concentrate was added.
7. The course of the reaction was followed by absorbing the H_2S in the caustic solution (designated as scrubber solution or off-gas absorber solution) and analyzing the solution periodically for its sulfide content.
8. In some runs the solution in the reaction vessel was sampled periodically, filtered, and analyzed for iron and copper.
9. The run was normally continued until the sulfide concentration in the scrubber solution (step 7 above) reached a constant level indicating dissolution of the iron in the acid was complete.
10. When the run was complete, the reaction slurry was filtered and the solid residue washed with water.
11. The solid residue was dried at 110°C, weighed and analyzed for iron, copper and sulfur. (In certain runs the residue was also analyzed for minor constituents.)
12. The filtrate and wash solutions were combined, diluted to a known volume and analyzed for iron and copper. (As in 11 above in certain runs the solution was analyzed for minor constituents.)
13. Material balances for the iron, copper and sulfur were then calculated based on the feed, solid residue, leach solution, and scrubber solution analyses.

After several runs it became apparent that the amount of H_2S liberated was a good measure of the iron dissolved (normally very little copper dissolved) and was the most reliable method of following the leaching reaction. For this reason in most of the runs no attempt was made to sample and analyze the leach solution during the course of the run. Only the final solution was analyzed for iron and copper.

Some runs were made at the boiling point of the hydrochloric acid. For 4N HCl this was about 106°C. Since temperature control was not critical, as long as the solution was boiling, the water bath was not needed. Instead the reaction vessel was heated directly using the stirring hot plate.

ANALYTICAL PROCEDURES

A variety of procedures was used to analyze the concentrates, neutral-roasted concentrates, leach solutions, leach residues and scrubber solutions. In addition, considerable use was made of a commercial assayer to analyze the concentrates, neutral-roasted concentrates and leach residues. Results obtained from the assayer were checked periodically by in-house analysis of duplicate samples. The assayer was employed for economic reasons. In-house analytical facilities could not compete on a cost basis with the assayer on routine analyses such as iron, copper and sulfur in concentrates.

The H_2S evolved during the leaching was determined by absorbing the H_2S in sodium hydroxide solution and analyzing the solution for sulfide ion.

$$H_2S + 2NaOH \longrightarrow 2Na^+ + S^= + 2H_2O$$

The sulfide content of the caustic solution was determined using a sulfide specific ion electrode (Orion Model 94-16A) and calomel reference electrode (Beckman Perma-Probe solid state reference electrode Model 39407). The following procedure was used.

> A known volume of the sulfide-caustic solution (usually 2-5 mls) was added to about 150 ml of 1M sodium hydroxide solution. The solution was thoroughly mixed using a magnetic stirrer. The sulfide sample was then titrated with 0.1M silver nitrate solution. The titration end point was determined using the sulfide electrode, reference electrode and a digital millivolt meter.

A typical titration curve is shown in Figure 3. The point of greatest inflection is taken as the end point. The procedure precision was found to be ±2.0%.

Iron in the leach solutions was determined using the procedure developed by Harvey, et al.(37) and a Cary Model 14H recording spectrophotometer. The procedure allows the simultaneous determination of both

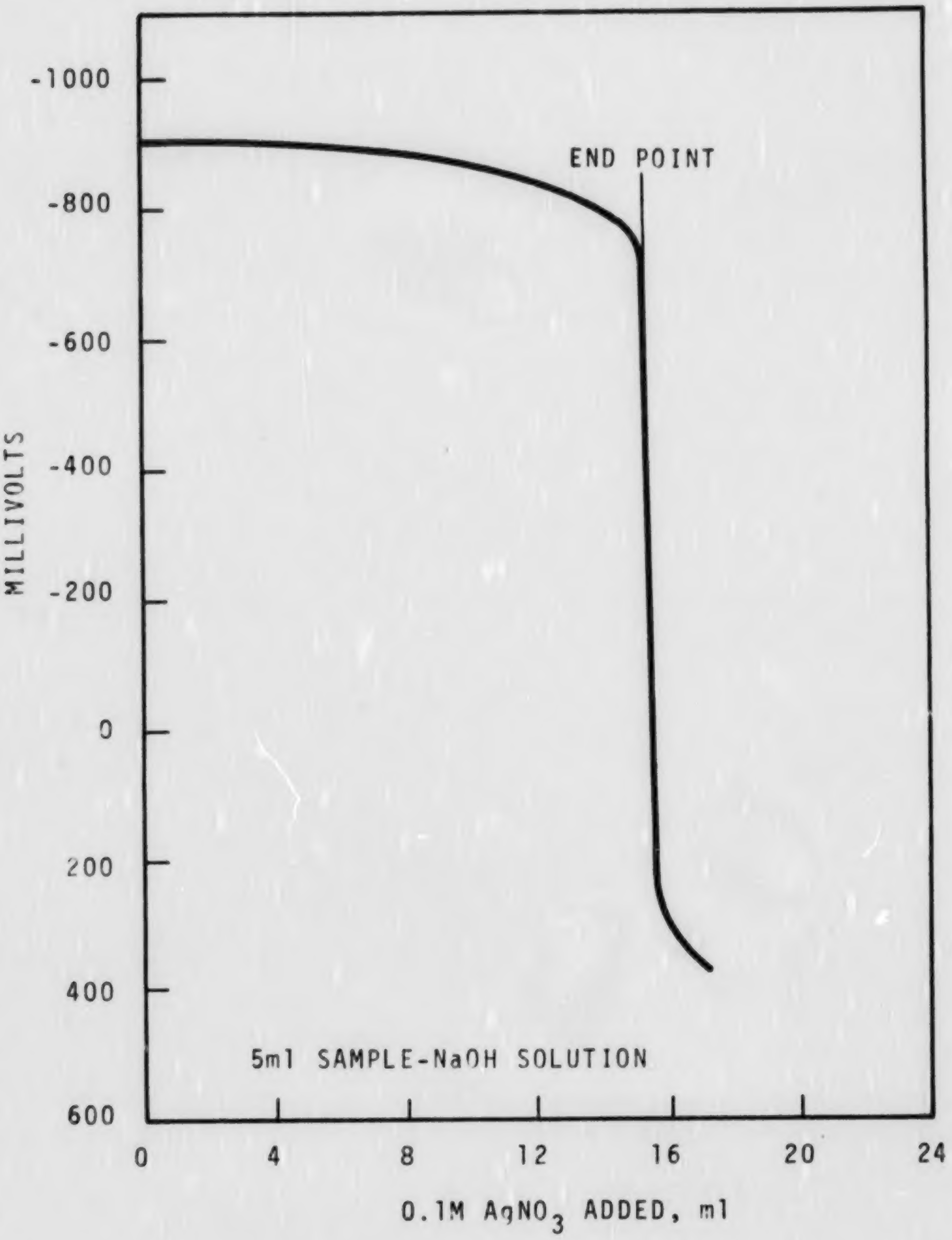

FIGURE 3. Typical Sulfide Titration Curve Using Sulfide Electrode

iron (II) and total iron in the solution. Iron (III) is obtained by difference. Impurities present in the leach solution, such as copper and chloride, do not interfere at the levels present. The procedure used is as follows:

> A known volume of leach solution (50-100 lambda) is placed in a 50 ml volumetric flask. Ten ml of 0.3% 1,10 phenanthroline and 5 ml of 0.2M potassium acid phthalate are added. Distilled water is added to the mark and the solution stirred. The absorbance of the solution is read (within 30 minutes) on the Cary at 396 mμ and 512 mμ. The precision of the procedure is about ±1.5%.

Preparation of the standard concentration curves is rather complex as is calculating the iron (II) and iron (III) from the curves. The reader is referred to the original reference(37) for complete details on the procedure.

Copper in the leach solutions was determined by atomic adsorption using standard procedures.

The procedures described above were also used to determine iron and copper in the concentrates, neutral-roasted concentrates and leach residues after they had been solubilized by fusion techniques. Sulfur in the solids was determined using the Leco SO_2 analyzer.

The various concentrates and neutral-roasted concentrates were analyzed by thermal techniques using the DuPont Model 990 Thermal Analyzer and Model 951 Thermogravimetric Analyzer.

RESULTS AND DISCUSSION

The basic steps in the proposed process were demonstrated on a laboratory scale. These included the neutral roasting, acid leaching, and copper recovery from the leach solution. Conversion of the ferrous chloride to ferric oxide and recovery of the hydrochloric acid was not studied in detail because commercial processes are available for this operation. To simplify the equipment required batch reactors were used for the neutral roasting and leaching operations. On a commercial scale, however, both operations would expect to be carried out in continuous reaction systems.

NEUTRAL ROASTING

Neutral roasting of the copper concentrates is necessary in order to carry out the acid leaching operation. When run-of-mill flotation concentrate is leached with hydrochloric acid there is very little reaction and no production of H_2S. When the concentrate (or pyrite) is heated to an elevated temperature (>500°C) in an inert atmosphere part of the sulfur is evolved and the residue obtained is partially soluble in hydrochloric acid. Almost all of the iron in the neutral-roasted concentrate dissolves forming ferrous chloride with the evolution of H_2S. The neutral-roasting operation is, therefore, a vital part of the overall process.

Substantial volumes of each concentrate were roasted under various conditions for use in the leaching studies. In addition, thermal analysis (DTA and TGA) was used to determine the optimum conditions for the neutral-roasting operation. Chemical and X-ray analysis were used to assess the composition of the neutral-roasted concentrates.

Composition of Neutral-Roasted Concentrates

When the concentrates are heated in an inert atmosphere (or vacuum) water and elemental sulfur (plus small amounts of H_2S and SO_2) are evolved. In a static system the amount of sulfur released will depend on the mineralogical composition, system temperature and the sulfur partial pressure (assuming equilibrium is attained). In a flowing system, where the sulfur is removed as it is formed, the amount of sulfur evolved will depend on the mineralogical composition, the reaction temperature and the time at temperature. The geometry of the concentrate bed can affect the efficiency of sulfur removal and thus affect the time required to achieve a given sulfur loss. This will be discussed in a later section.

For the leaching studies, the bulk of the concentrates were neutral-roasted at 800°C in flowing argon or helium (no differences in product composition were detected as a result of interchanging the inert gases). They were processed in one-kilogram batches. Where more than one kilogram of a given concentrate had to be treated, several batches were processed and the products combined and blended by ball milling. The compositions of the neutral-roasted concentrates, prepared at 800°C, are presented in Table II. It is impossible to assign specific formulas to the neutral-roasted concentrates. However, ignoring the minor constituents, the neutral-roasted products have composition ratios as listed following Table II.

TABLE II. Composition of Neutral Roasted Concentrates

Concentrate	Temp. (°C)	Atmosphere	Time at Temp. (hrs)	Product Composition, wt%		
				Fe	Cu	S
Morenci	800	Argon	24	33.4	24.7	28.8
Pima	800	Argon	24	29.4	29.4	27.8
Anaconda	800	Argon	24	23.2	34.9	26.5
Tyrone	800	Helium	16	36.4	23.9	28.6
Battle Mtn	800	Helium	16	28.1	28.1	24.9
Lavender Pit	800	Helium	16	39.1	15.4	29.0
San Manuel	800	Helium	24	28.5	32.5	26.7
Hecla (pyrite)	800	Helium	24	52.9	--	33.9

Concentrate	Composition	Fe+Cu/S
Morenci	$Fe_{1.33}Cu_{0.86}S$	$(M_{1.10}S)$
Pima	$Fe_{1.21}Cu_{1.07}S_2$	$(M_{1.14}S)$
Anaconda	$Fe_{1.01}Cu_{1.33}S_2$	$(M_{1.17}S)$
Tyrone	$Fe_{1.46}Cu_{0.84}S_2$	$(M_{1.15}S)$
Battle Mtn	$Fe_{1.29}Cu_{1.14}S_2$	$(M_{1.22}S)$
Lavender Pit	$Fe_{1.55}Cu_{0.54}S_2$	$(M_{1.05}S)$
San Manuel	$Fe_{1.22}Cu_{1.23}S_2$	$(M_{1.23}S)$
Hecla	$FeS_{1.12}$	

Comparing these compositions with those for the concentrates reported earlier one can see how the metal-sulfur ratio changes due to sulfur loss during neutral roasting.

	Concentrate	Neutral Roasted Concentrate
Morenci	$M_{0.73}S$	$M_{1.10}S$
Pima	$M_{0.99}S$	$M_{1.14}S$
Anaconda	$M_{0.72}S$	$M_{1.17}S$
Tyrone	$M_{0.69}S$	$M_{1.15}S$
Battle Mtn	$M_{0.92}S$	$M_{1.22}S$
Lavender Pit	$M_{0.63}S$	$M_{1.05}S$
San Manuel	$M_{1.04}S$	$M_{1.23}S$
Hecla	$FeS_{2.09}$	$FeS_{1.12}$

By neutral roasting at temperatures above 800°C sulfur removal can be increased. Table III shows the composition of Morenci concentrate which was neutral roasted at various temperatures. While there are some variations it is apparent that high temperatures and/or long reaction times

TABLE III. Effect of Temperature on Composition of Neutral Roasted Morenci Concentrate

Sample No.	Temp. °C	Time (hrs)	Atmosphere	Product Composition, wt%		
				Fe	Cu	S
1	800	24	Argon	33.4	24.7	28.8
2	800	16	Argon	32.3	23.7	29.2
3	860	20	Helium	32.1	24.6	27.0
4*	970	3	Vacuum	37.3	28.5	30.5
5**	1005	20	Vacuum	33.5	25.9	25.2

Ignoring the minor constituents the samples have the following compositions:

Sample No.	Composition	Fe+Cu/S
1	$Fe_{1.33}Cu_{0.86}S_2$	$M_{1.10}S$
2	$Fe_{1.27}Cu_{0.82}S_2$	$M_{1.05}S$
3	$Fe_{1.37}Cu_{0.92}S_2$	$M_{1.15}S$
4	$Fe_{1.40}Cu_{0.94}S_2$	$M_{1.17}S$
5	$Fe_{1.42}Cu_{1.04}S_2$	$M_{1.23}S$

---

* Product consisted of two phases: a solid mass (∿ 40 wt%) which had fused and a sintered mass. The analysis given is for the fused portion.

** Product had fused.

increase the metal-to-sulfur ratio of the neutral-roasted concentrates. Similar data for neutral-roasted Pima and Anaconda concentrates are given in Table IV.

TABLE IV. Composition of Neutral Roasted Pima and Anaconda Concentrates Prepared at Various Temperatures

Concentrate	Temp. (°C)	Time (hrs)	Atmosphere	Product Composition, wt%			M/S
				Fe	Cu	S	
Pima	800	24	Argon	29.4	29.4	27.8	$M_{1.14}S$
Pima* A	860	72	Vacuum	28.9	28.6	24.6	$M_{1.25}S$
B	860	72	Vacuum	29.1	30.9	25.5	$M_{1.27}S$
Pima	970	18	Vacuum	28.9	29.7	24.7	$M_{1.28}S$
Pima	1005	6	Vacuum	29.1	29.3	24.8	$M_{1.27}S$
Anaconda	800	24	Argon	23.2	34.9	26.5	$M_{1.17}S$
Anaconda	1000	4	Vacuum	28.1	42.3	26.9	$M_{1.39}S$

---

* Product consisted of two phases: (A) a partially sintered easily crushed powder, and (B) a highly sintered hard mass. The phases were separated and analyzed individually.

The physical characteristics of the neutral roasted concentrates varied with the reaction temperature and time at temperature. Concentrate processed at 800°C consisted of partially sintered easily crushed lumps and powder. Those heated to 1000°C or higher had partially fused and were more difficult to crush and grind. Concentrates processed at intermediate temperatures varied from loosely sintered powders to fused lumps depending on the time and temperature. The Pima concentrate showed a somewhat greater tendency to sinter than the others.

The particle size distribution of the Morenci concentrate, which had been roasted at 800°C for 24 hours in argon and then ball milled, was determined using U.S. Standard Sieve Series Screens. The distribution was as shown in the following:

Screen Size	Cumulative % Retained
+ 70	0.08
+100	6.04
+140	21.78
+200	47.84
+230	72.35
+325	89.96
Total	100.00

The material had a tap density of 2.34 g/cm^3, and the surface area was <0.5 sq m/gram.

X-Ray Analysis of Neutral-Roasted Concentrates

The various neutral-roasted concentrates were analyzed by X-ray diffraction in an attempt to identify the minerals present. These attempts met with only marginal success and it was impossible to identify, with certainty, the minerals present in the neutral roasted concentrates. A detailed study of the mineralogical composition of the neutral-roasted concentrates was beyond the scope of this program.

The iron-copper-sulfur system is extremely complex. Despite decades of investigation by many different workers the phase diagram for the system has not yet been completely defined.(5-25) Table V is a list of most of the minerals (stable at low temperatures) reported in the literature for the Fe-Cu-S system.(5) It does not include questionable or incompletely described minerals which have been reported. Figure 4 shows the Fe-Cu-S system and location in the diagram of the various minerals listed in Table V. The locations of the neutral-roasted concentrates (ignoring the minor constituents) are also indicated.

TABLE V. Compounds in the Fe-Cu-S System that are Stable at Low Temperatures(5)

Symbol	Name	Formula
a-bn	anomalous bornite	Cu_5FeS_4
an	anilite	$C_{1.75}S$
bbcv	blaubleibender covellite	$Cu_{1.1}S$
bn	bornite	Cu_5FeS_4
cc	chalcocite	Cu_2S
cf	chalcopyrite	$CuFeS_2$
cv	covellite	CuS
cb	cubanite	$CuFe_2S_3$
di	digenite	Cu_9S_5
dj	djurleite	$Cu_{1.96}S$
fk	fukuchilite	Cu_3FeS_8
gr	greigite	Fe_3S_4
hc	haycockite	$Cu_4Fe_5S_8$
h-po	hexagonal pyrrhotite	Fe_9S_{10}
ld	Idaite	Cu_3FeS_4
mk	mackinawite	$Fe_{1.06}S$
ma	marcasite	FeS_2
mh	mooihoekite	$Cu_9Fe_9S_{16}$
m-po	monoclinic pyrrhotite	Fe_7S_8
py	pyrite	FeS_2
sm	smythite	Fe_3S_4, $Fe_{3.34}S_4$
tal	talnakhite	$Cu_9Fe_8S_{16}$
tr	troilite	FeS
?	probable new mineral	Cu_5FeS_6
??	new mineral	$Cu_{0.12}Fe_{0.94}S$
s	synthetic mineral	$Cu_3Fe_4S_6$

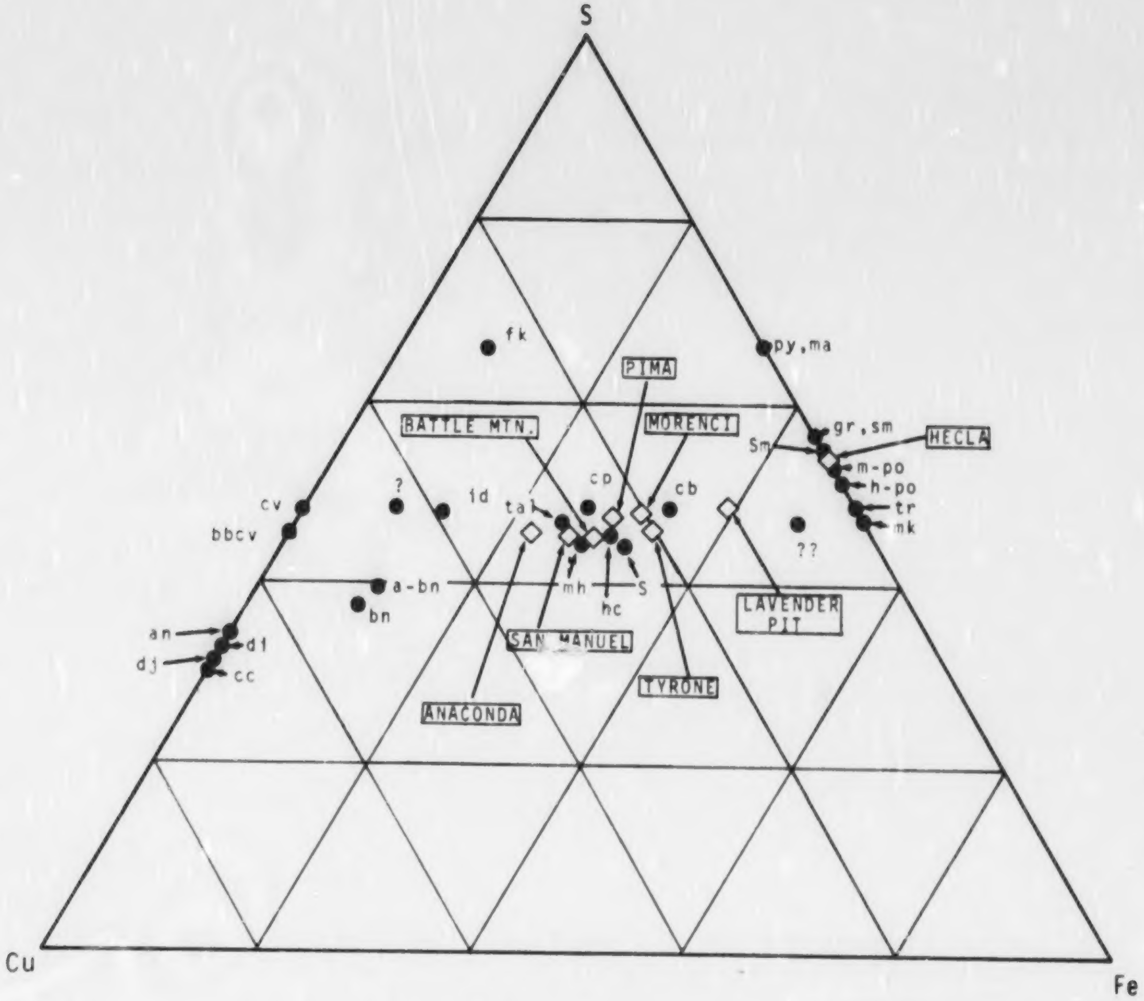
S
fk
py,ma
PIMA
BATTLE MTN.
MORENCI
gr,sm
HECLA
Sm
m-po
h-po
tr
mk
cv
bbcv
?
id
cp
cb
ta
??
a-bn
bn
mh
hc
S
LAVENDER PIT
SAN MANUEL
TYRONE
ANACONDA
an
di
dj
cc
Cu
Fe

FIGURE 4. Mineral Compositions in the Fe-Cu-S System (See Table V for meaning of symbols.)

The compositions of the neutral roasted concentrates (except for the Hecla) fall in the central area of the Fe-Cu-S system. Cabri,(5) Yund and Kullerud(24) and others have shown that at elevated temperatures the central area of the Fe-Cu-S system is characterized by a large solid solution field. The composition of the neutral roasted copper concentrates place them within the solid solution field at temperatures of 700°C and above. According to Cabri(5) "The central area of the Cu-Fe-S system is characterized by a large solid solution field at elevated temperatures which breaks up into five distinct phases at low temperatures. The picture is complicated by numerous phase transformations, unquenchable phases, and phases with closely related crystal chemistry, resulting in their having similar physical appearance and X-ray diffraction powder patterns. The slow rate of most of the reactions at low temperatures also makes it difficult (in some cases impossible) to achieve equilibrium in the laboratory." This statement helps explain the difficulties encountered in trying to identify phases present in the neutral roasted concentrates. When the concentrates were neutral-roasted they were held at temperature for limited periods of time (4-24 hours). It is not known if this time was sufficient for solid solution to occur. In addition, no attempts were made to control the quench rate when the concentrates were cooled. Therefore samples of a given concentrate which were neutral-roasted under approximately similar conditions could have different mineralogical compositions depending on such factors as variations in cooling rate. For example, four samples of air dried Morenci concentrate were heated to 800°C in flowing helium on the thermobalance and then cooled to room temperature. The cooling rate used was the normal cooling rate of the thermobalance furnace with the power off (approximately 90 minutes from 800 to 50°C). The samples were then analyzed by X-ray diffraction. The diffraction patterns for the four samples are presented in Table VI. It is readily apparent that there are significant differences between the patterns as well as great similarity. The lines of highest intensity are very similar for all four samples. Similar results were observed with the Pima and Anaconda concentrates.

TABLE VI. The X-Ray Diffraction Patterns for Samples of Morenci Concentrates which were Neutral Roasted at 800°C in Flowing Argon on the Thermobalance

Sample No. SM-1		Sample No. SM-2		Sample No. SM-3		Sample No. SM-4	
dA°	I/I_o	dA°	I/I_o	dA°	I/I_o	dA°	I/I_o
6.46	15	6.50	15	6.50	30	6.42	10
3.37	20	4.56	15	3.37	20	3.36	15
3.28	25	3.36	10	3.30	25	3.11	100
3.16	25	3.15	100	3.15	45	2.68	10
3.09	100	3.09	55	3.11	100	2.10	10
3.01	20	3.01	10	3.00	25	1.89	55
2.75	25	2.90	10	2.75	20	1.61	20
2.67	30	2.78	10	2.67	30	1.45	5
2.51	15	2.66	20	2.54	15	1.33	5
2.37	20	2.08	25	2.10	45	1.23	10
2.09	35	1.93	20	1.93	50	1.09	10
1.97	20	1.89	30	1.89	55	1.03	5
1.94	35	1.81	10	1.75	20		
1.93	40	1.73	15	1.61	30		
1.89	70	1.61	15	1.33	20		
1.73	20	1.57	10	1.15	15		
1.64	20	1.33	5	1.11	15		
1.61	35			1.09	15		
1.33	20						
1.22	15						
1.11	15						
1.09	20						
1.03	20						

Samples of neutral-roasted Pima which were prepared at different temperatures exhibited completely different X-ray diffraction patterns (see Table VII). Samples of neutral-roasted Anaconda prepared at different temperatures also showed a lack of similarity in their diffraction patterns. In the case of neutral-roasted Morenci the situation was different. The samples prepared at different temperatures had similar but not identical diffraction patterns.

TABLE VII. X-Ray Diffraction Patterns for Neutral Roasted Pima Concentrate Prepared Under Various Conditions

Sample P-1*		Sample P-8**	
dA°	I/I_o	dA°	I/I_o
3.40	15	6.31	30
3.10	100	3.30	30
2.67	15	3.15	60
1.89	80	3.10	30
1.61	30	3.00	40
1.55	5	2.72	30
1.34	10	2.67	40
1.33	10	2.53	10
1.31	10	2.10	85
1.22	5	1.93	100
1.09	10	1.75	20
		1.73	35
		1.64	20
		1.33	5
		1.09	5

---

* Concentrate neutral roasted for 24 hours at 800°C in inert atmosphere.

** Concentrate neutral roasted for 6 hours at 1005°C under vacuum.

It was not possible to identify, with complete confidence, specific mineral phases in any of the neutral roasted concentrates. None of the X-ray diffraction patterns obtained could be attributed specifically to known patterns published in the ASTM Powder Diffraction File.

In the case of the neutral-roasted Morenci and Pima concentrates prepared at 800°C their diffraction patterns were similar, but not identical, to those reported for mooihoekite ($Cu_9Fe_9S_{16}$) and talnakhite ($Cu_9Fe_8S_{16}$).(5,7,8,10) The two materials probably contain either or both minerals. It is also possible they may contain some cubanite ($CuFe_2S_3$).

In the case of neutral roasted Anaconda concentrate prepared at 800°C, the X-ray diffraction pattern could not be identified with any published patterns for the Fe-Cu-S system. The material prepared at 1000°C had a distinctly different pattern. The pattern had a slight similarity to the patterns for cubanite ($CuFe_2S_3$) and bornite (Cu_5FeS_4), and the material could be a mixture of the two minerals.

The bulk of the leaching tests were carried out with concentrates which were neutral-roasted at 800°C. In the case of the Morenci, Pima and Anaconda, several batches of each concentrate were roasted at 800°C and blended. The blended lot of each concentrate was used for the leaching tests. Therefore, differences in mineral composition from batch to batch due to slight uncontrolled variations in the neutral roasting operation would be masked by the blending operation.

Thermal Analysis of Concentrates

The neutral roasting of concentrates was studied using differential thermal analysis and thermogravimetric analysis. Thermograms were obtained for the various concentrates in purified helium. Figure 5 shows weight loss as a function of sample temperature for Morenci, Pima, and Anaconda concentrates when heated in helium. The thermograms for the other concentrates are shown in Figure 6. The initial weight loss (up to a temperature of about 350°C) is due to the vaporization of water. At higher temperatures

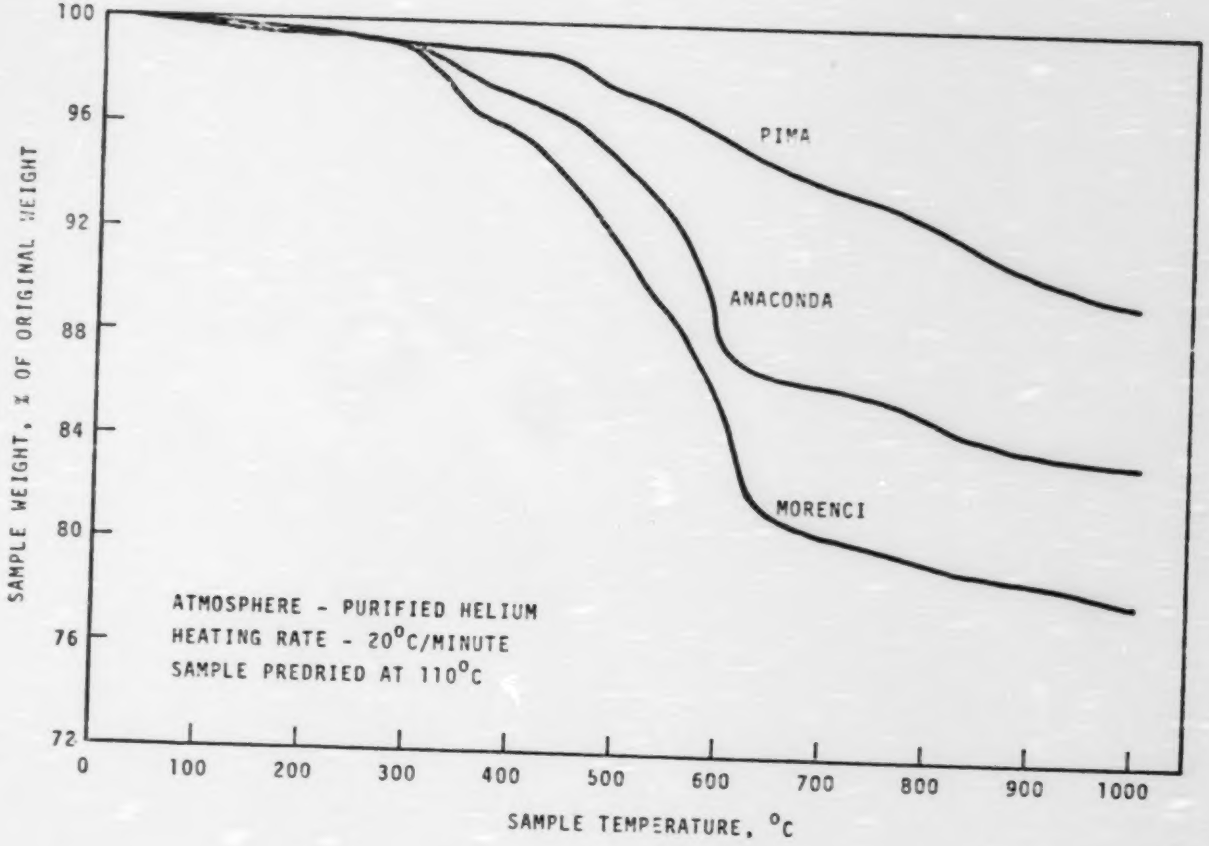

FIGURE 5. Thermogravimetric Analysis of Copper Concentrates in Helium

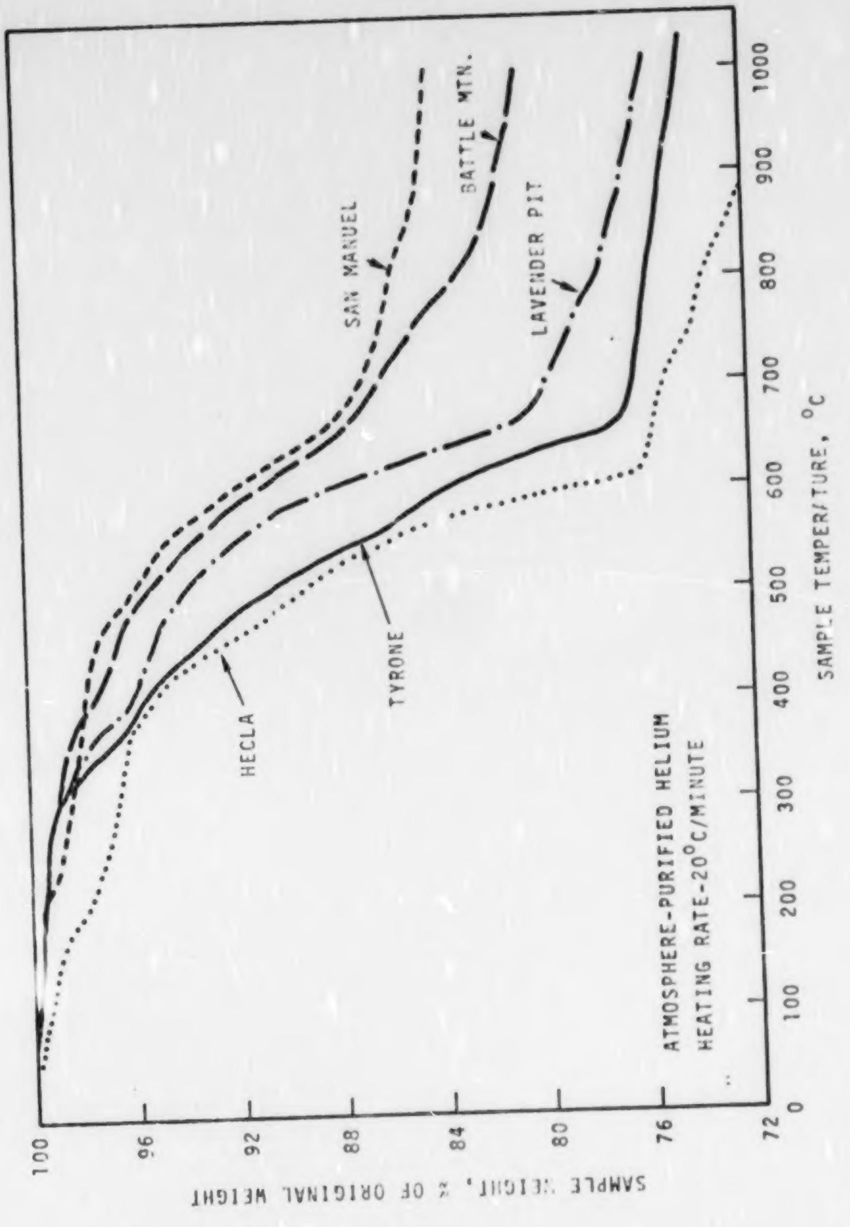

FIGURE 6. Thermograms for Concentrates in Helium

the weight loss is due to the evolution of sulfur (and small amounts of H_2S and SO_2). In the case of the Anaconda concentrate a fraction of the weight loss is due to vaporization of arsenic sulfide and possibly zinc sulfide.

The data presented in Figures 5 and 6 were obtained at a heating rate of 20°C/minute. To show the effect of heating rate on the decomposition reaction(s) samples of Morenci concentrate were heated at various rates. The results obtained are presented in Figure 7.

To obtain a better measure of the kinetics of the decomposition reaction samples of Morenci concentrate were inserted into a preheated furnace and the weight loss followed as a function of time. The thermograms obtained are shown in Figure 8. It normally required from 1 to 2 minutes for the sample to reach the reaction temperature. During this heat-up time, considerable sulfur evolution occurred, especially when the control temperature was above 500°C. It was impossible, therefore, to measure precisely the evolution of sulfur as a function of time at temperature. In obtaining the data presented in Figure 8 the sample temperature was monitored as a function of time as well as sample weight. The dashed portions of the thermograms represent the periods in which sample temperatures were increasing to the control temperatures. It can be seen from the data that a substantial fraction of the weight loss occurred before the control temperature was reached. At temperatures of 600°C and above most of the weight loss occurs in the first 25-50 minutes. Thereafter the loss of weight continues at a slow, almost constant, rate for long periods of time. One run at 800°C, using Morenci concentrate, was continued for 24 hours; a continual weight loss was observed throughout the run. The overall weight loss at the end of the 24 hour period was 26.06%. The weight change observed during the last few hours of the run was so slight, however, it may have been due to instrument instability.

The thermobalance data were obtained using platinum pans with a thin layer of concentrate spread over the pan surface. Under these conditions the sulfur formed was easily removed from the reaction zone by the flowing

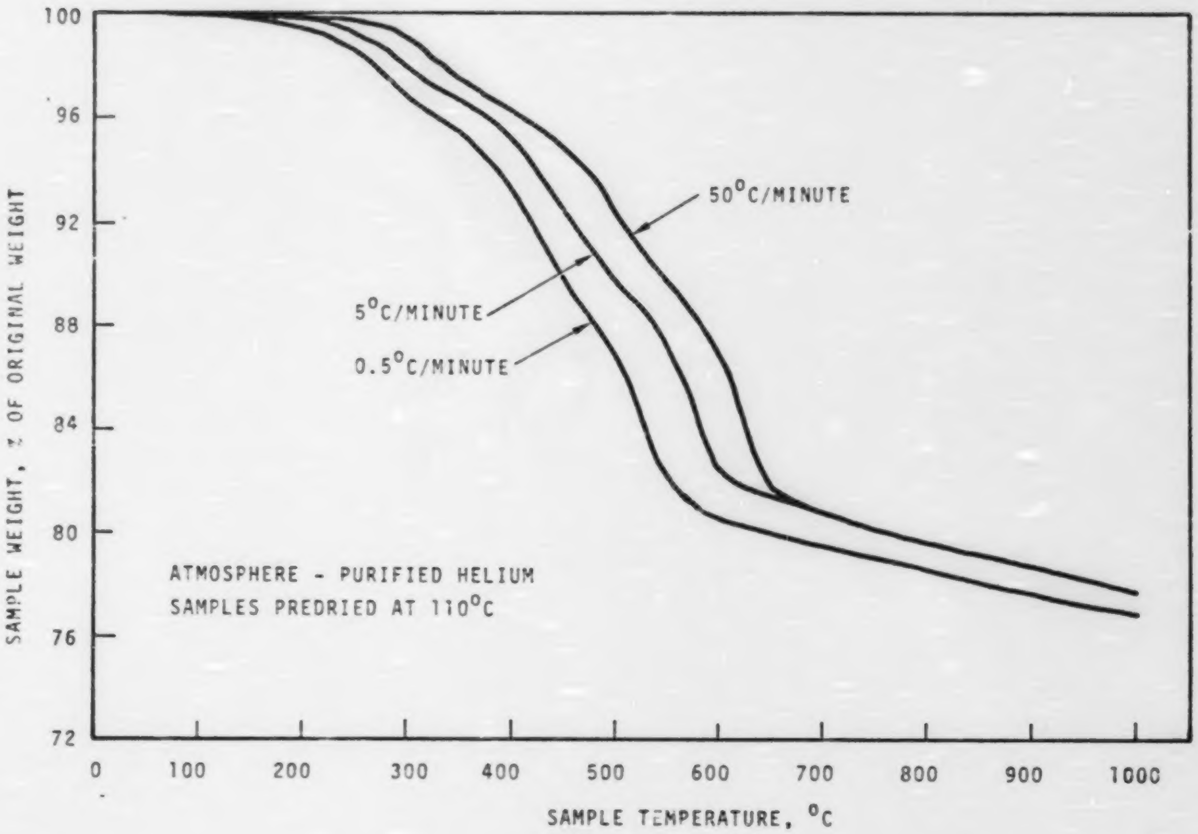

FIGURE 7. Effect of Heating Rate on the Thermal Decomposition of Morenci Concentrate

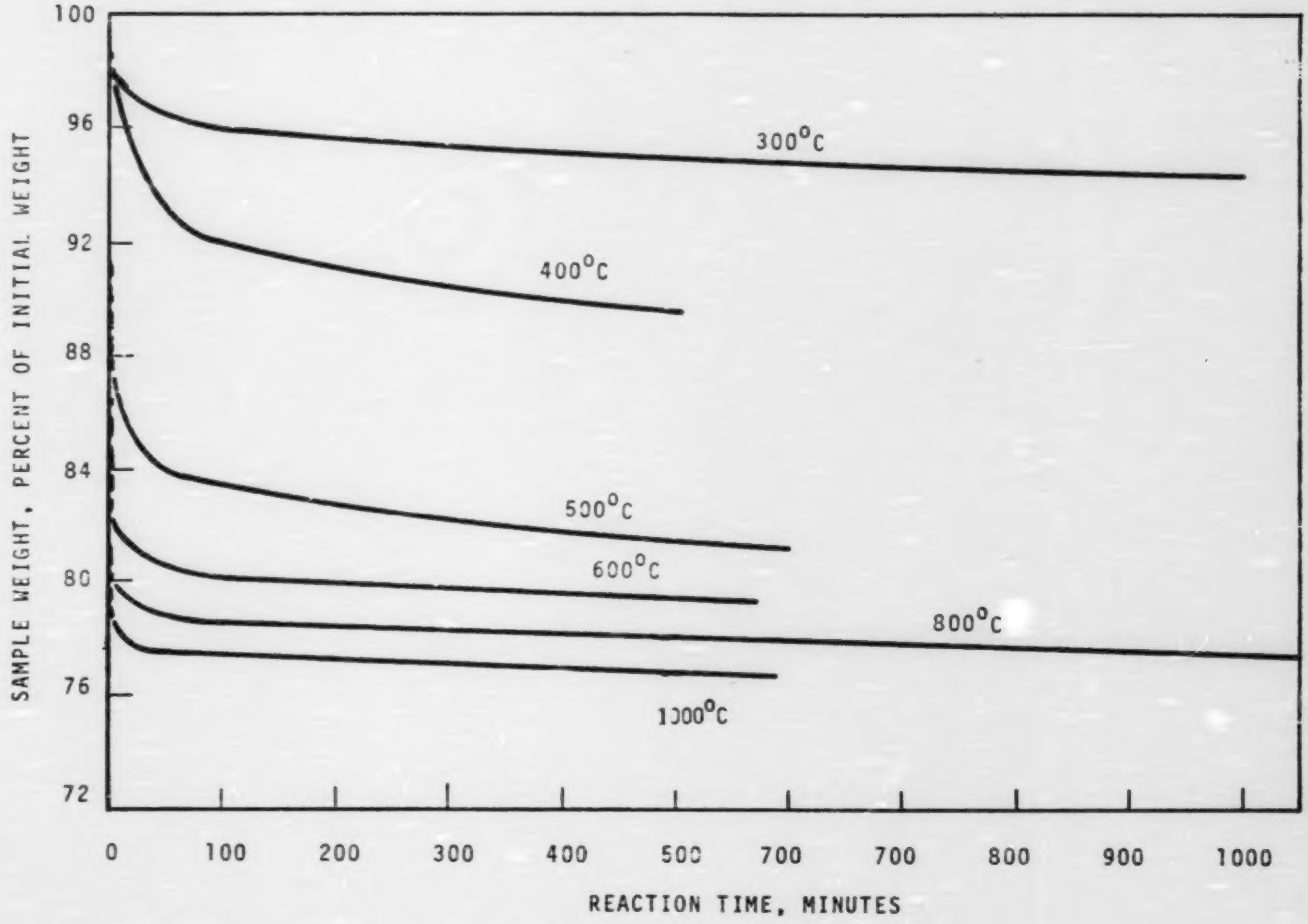

FIGURE 8. Effect of Temperature on Roasting of Morenci Concentrate

helium. When the bulk samples of concentrate were neutral-roasted the situation was different. In the horizontal tube reactor the depth of concentrate in the tube was up to 1.5 inches and the bed was 8-12 inches long. The argon purge gas tended to flow over rather than through the bed. Under these conditions sulfur removal from the reaction zone was poor. The same situation existed in the pot reactor where the depth of concentrate was several inches. Because removal of the sulfur was so poor with the bulk samples they had to be heated for many hours to achieve the same weight loss that was observed on the thermobalance in an hour or less.

Each of the concentrates was analyzed by differential thermal analysis. Thermograms obtained with the Morenci, Pima, and Anaconda concentrates in argon are shown in Figure 9. In each case the endothermic reactions up to about 350°C correspond to loss of water from the sample. The endothermic reactions between 400 and 700°C correspond to the decomposition reactions which evolve sulfur (and H_2S and SO_2). Above 700°C the major endothermic reactions probably correspond to solid phase changes and/or sample melting. It is fairly certain that the endotherms at 950-975°C correspond to melting. The exotherms which occur on cooling at 950-900°C result from freezing: while in the case of the Anaconda the exotherm at 740°C on cooling is probably a solid phase transition. The thermograms for the other concentrates are similar to those obtained with the Morenci, Pima, and Anaconda concentrates.

A better understanding of the reactions involved can be obtained by comparing the DTA and TGA data for a given concentrate. DTA and TGA plots obtained with Morenci concentrate in purified helium at a heating rate of 5°C per minute are shown in Figure 10. The initial endotherms (up to 350°C) correspond to the initial weight loss due to vaporization of water. The large endothermic reaction between 400 and 700°C corresponds to the maximum sample weight loss (evolution of sulfur). The endothermic reactions above 700°C are reversible and indicate a phase change of one or more constituents of the concentrate. Some weight loss occurs above 700°C but this would not account for the endothermic reactions observed.

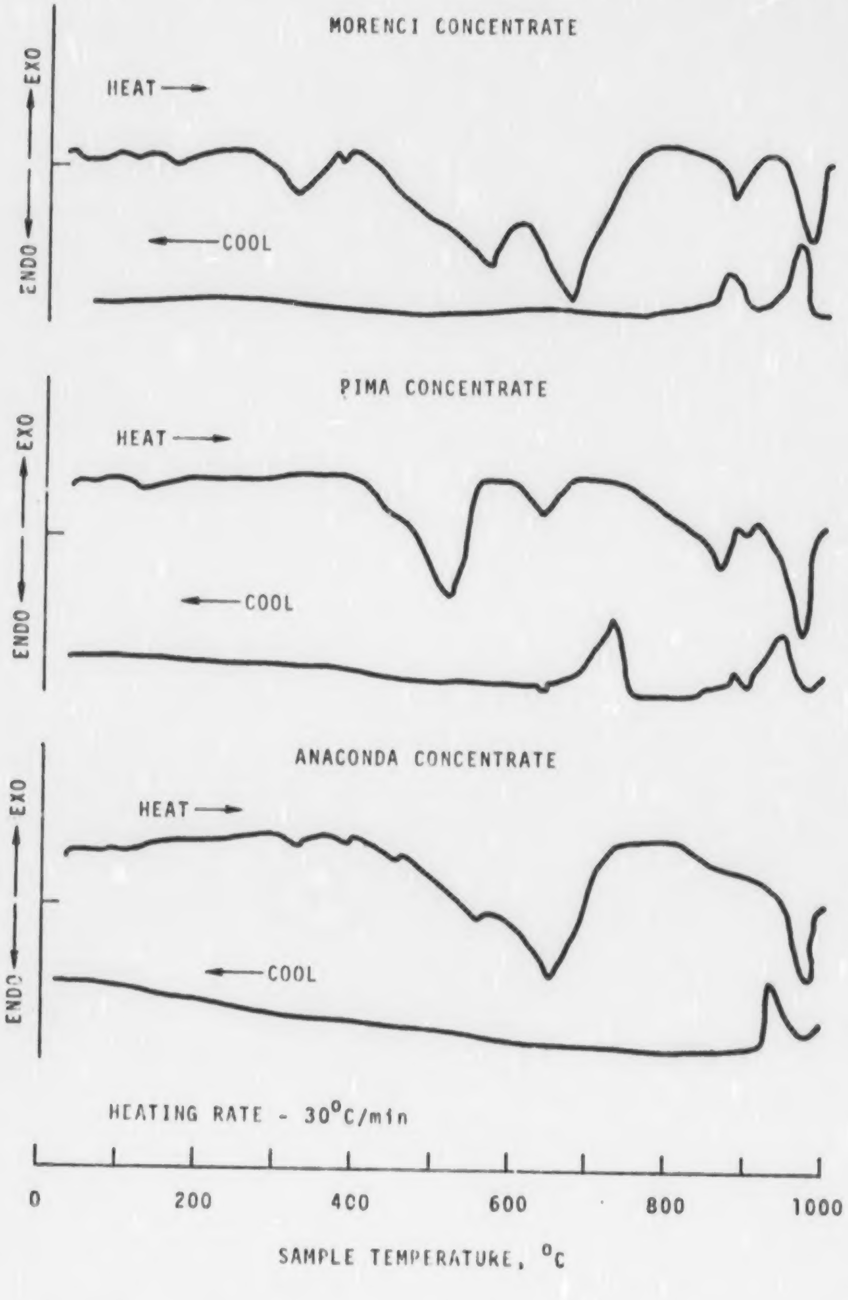

FIGURE 9. Differential Thermal Analysis Curves for Copper Concentrates Heated in Purified Helium

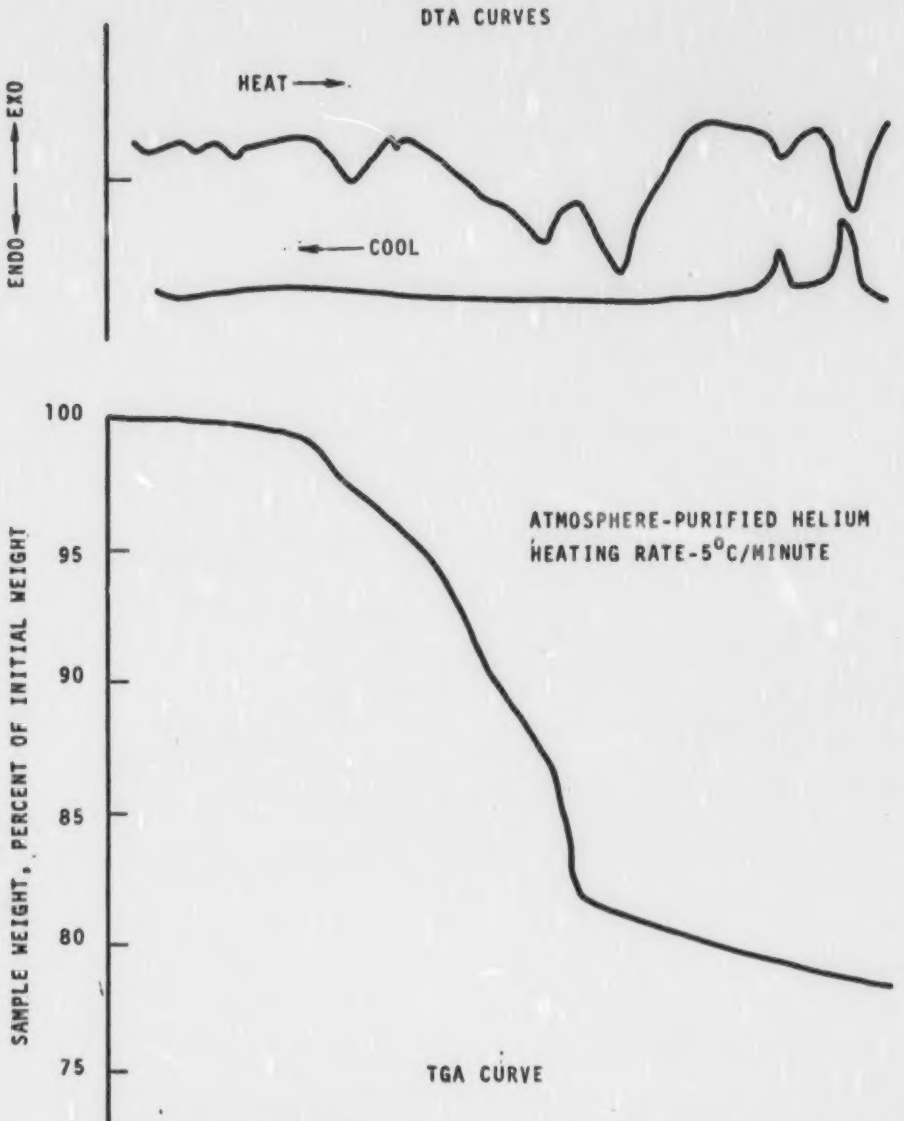

FIGURE 10. Thermograms for Morenci Concentrate

Trace Impurities

The copper concentrates contain a number of trace impurities which can play a significant part in a commercial process. Some of the concentrates contain significant precious metal values (Anaconda and Battle Mountain). Others contain impurities which can represent a safety problem and their fate during the various process operations must be known. The Anaconda concentrate is one which contains significant levels of impurities; it was used to determine the fate of impurities during neutral roasting. The concentrate was neutral-roasted for 24 hours in flowing argon. The product was then analyzed for impurities. The results are shown in Table VIII, together with the analyses of the original concentrate. To account for the weight loss encountered during neutral-roasting the impurities are reported as grams per 100 grams of original concentrate.

TABLE VIII. Effect of Neutral Roasting at 800°C on the Impurities in Anaconda Concentrate

	Grams per 100 Grams of Original Concentrate	
Impurity	Concentrate	Neutral Roasted Concentrate
As	1.86	0.17
Sb	0.037	0.06
Zn	6.2	3.76
Pb	0.05	0.2
Mo	0.05	0.064
Bi	0.03	0.032
Cd	0.12	0.50
Se	0.029	0.018
Te	0.025	0.0056
Hg	0.024	0.00016
Ag*	10.42	10.2
Au*	0.07	0.051

---

* In troy ounces per ton of original concentrate.

From the results it can be seen that the bulk of the arsenic in the concentrate is volatilized during roasting and should end up in the sulfur. A fraction of the zinc also appears to have volatilized, probably as the sulfide. Conflicting results were obtained with some of the trace level impurities. With some elements (i.e., Sb, Pb, Cd) the analytical results show a greater amount in the neutral-roasted concentrate than in the feed, clearly an impossibility. This is due to lack of precision of the analytical method at very low concentrations. All that can be said is that the neutral-roasted concentrate contains a certain amount of the impurity but the exact level cannot be defined. In the case of gold and silver the analyses agree, within the procedure precision, and essentially all of the gold and silver in the concentrate end up in the neutral-roasted concentrate. This is a desirable situation because it assures that the precious metals will be recovered from the concentrate by the usual techniques in the subsequent conventional processing steps of converting and electrolytic refining.

Sulfur Dioxide Formation

When the copper concentrate is neutral roasted, some H_2S and SO_2 are formed. When the gas stream from the reactor cools the H_2S and SO_2 combine to form elemental sulfur. However, the off-gas always contains more SO_2 than is required to react with the H_2S; thus cold off-gas always contains some SO_2.

The exact mechanisms by which the SO_2 and H_2S are formed have not been determined, but they probably result from the reaction of water in the concentrate with the concentrate and/or elemental sulfur. This hypothesis is strengthened by the fact that reducing the water content of the concentrate prior to neutral roasting reduces the amount of SO_2 formed during roasting.

No attempt was made to determine the amount of SO_2 and H_2S formed during neutral-roasting, but the excess SO_2 in the off-gas was measured for Morenci concentrate. When the concentrate is neutral-roasted at 800°C in flowing helium, approximately 1.2% of the sulfur in the concentrate shows up as free SO_2. The SO_2 yield was approximately the same when the concentrate was neutral-roasted at 1000°C. The concentrate used in these tests contained about 3.5% water. When the concentrate was dried under vacuum at 170°C, the water content was reduced to about 1.5%. When this material was neutral-roasted at 800°C the free SO_2 formed amounted to about 0.8% of the sulfur in the concentrate.

To determine the effect of a reducing atmosphere on the decomposition reaction and SO_2 formation, Morenci concentrate was roasted in an atmosphere of Argon-4% Hydrogen at 800°C. Use of a reducing atmosphere increased the excess SO_2 in the off-gas to about 2.1% of the sulfur in the concentrate. The composition of the neutral-roasted concentrate was not changed significantly from that obtained in argon.

Two samples of Morenci concentrate were also roasted at 800°C in He-2% O_2. The amount of SO_2 formed was substantially increased, and the final products were magnetic. The composition of the two products were:

	Sample No. 1	Sample No. 2
Fe	31.8 wt%	32.86 wt%
Cu	24.2	24.6
S	26.4	26.7
	$Fe_{1.38}Cu_{0.93}S_2$	$Fe_{1.42}Cu_{0.93}S_2$
	$M_{1.15}S$	$M_{1.17}S$

The sulfur content of the samples is lower than usual and it is probable that some oxidation of the samples occurred, possibly with some sulfate formation. The H_2S evolved when these materials were treated with HCl was also greatly reduced. This is convincing evidence that the iron sulfide had been oxidized.

When pyrite was neutral-roasted, about 1.5% of the sulfur in the pyrite was evolved as SO_2. Work reported by others(29) indicated much higher SO_2 formation as well as some COS formation when pyrite was neutral-roasted. Reasons for the discrepancies between the studies have not been developed.

ACID LEACHING

The leaching of neutral roasted concentrates in hydrochloric acid was studied in considerable detail using a batch reaction system. The principal reaction involved is the dissolution of iron sulfide to form ferrous chloride and hydrogen sulfide. The amount of ferric chloride formed was usually very low. The effects of the following variables on the reaction were evaluated:

1. concentrate type (i.e., Morenci, Pima, etc.)
2. concentrate composition variations (due to temperature and time for roasting)
3. reaction temperature
4. acid concentration
5. acid-concentrate ratio

Two variables which were not studied were stirring rate and concentrate surface area. An attempt was made to use the same stirring rate for each experiment, but the variations in H_2S yield and iron dissolution observed in duplicate runs may reflect variations in stirring rate. Because the reaction involved is a liquid-solid reaction, stirring would have less effect on the kinetics than if a gas-solid reaction were occurring as in the case of oxidative leaching reactions involving the use of oxygen. No attempt was made to study the effect of concentrate surface area on the leaching reaction. The only control used was to insure the neutral roasted concentrates used in the leach tests were all -70 mesh in particle size.

The progress of a given leaching experiment was followed by measuring the H_2S evolved. In some runs the leach solution was sampled periodically and analyzed for iron and copper. Figure 11 shows typical data obtained with neutral-roasted Morenci concentrate and a reaction temperature of 106°C (boiling point of 4N hydrochloric acid). By analyzing the feed material, leach solution, solid residue and off-gas absorber solution material balances for iron, copper and sulfur were calculated for the leaching reaction. Material balance data for a typical leaching experiment are shown in Table IX.

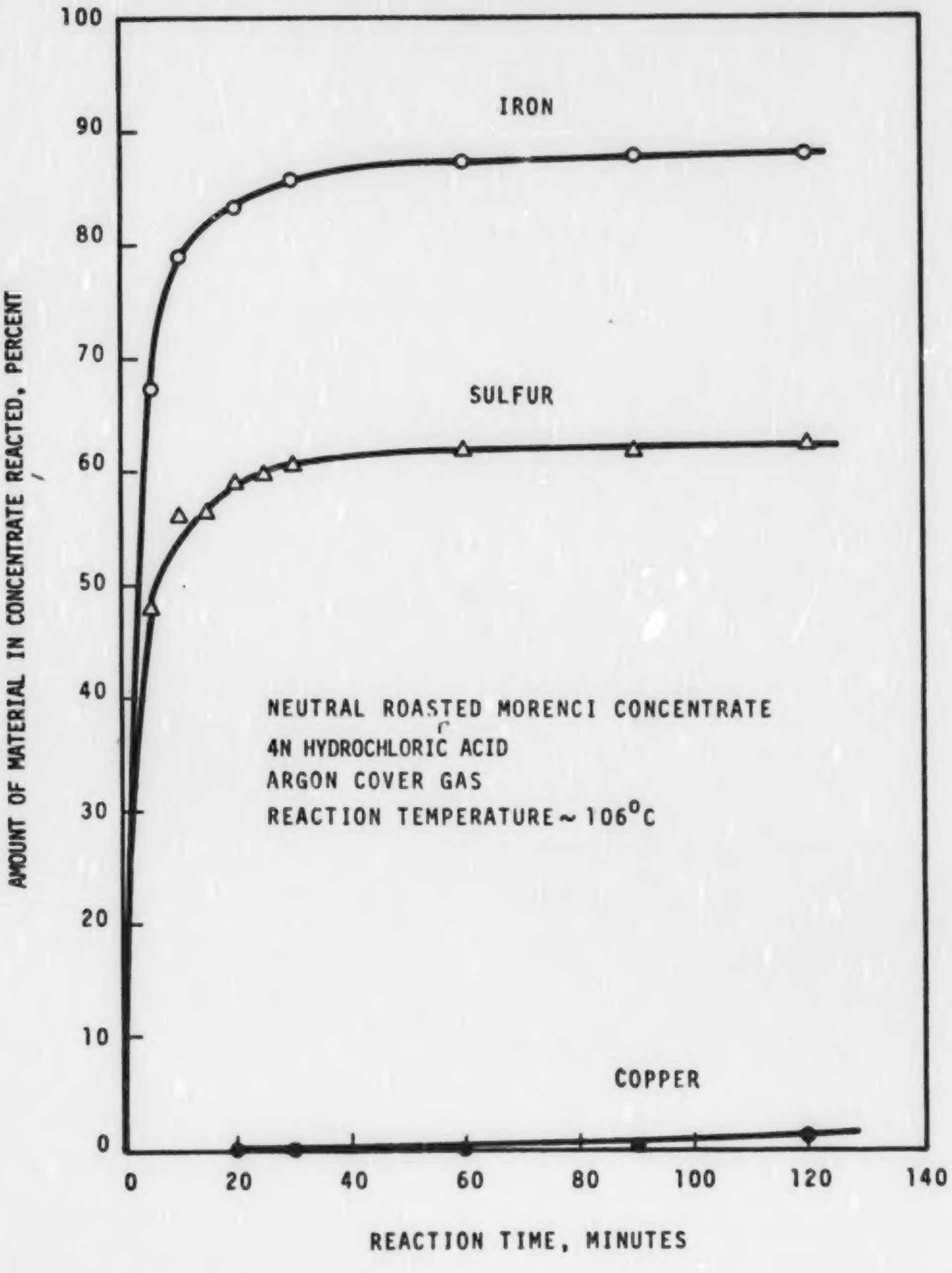

FIGURE 11. Typical Leaching Data for Neutral Roasted Morenci Concentrate

TABLE IX. Material Balance Data for a Typical Leaching Experiment Using Neutral Roasted Morenci Concentrate

Reaction Conditions:
50.0 grams neutral roasted concentrate
300 ml 4N hydrochloric acid
Reaction temperature - 80°C
Reaction time - 150 minutes

Feed Analysis:
Fe = 33.36% (16.68 grams)
Cu = 24.66% (12.33 grams)
S = 28.8% (14.40 grams)

Residue Analysis:
Amount of residue = 21.6 grams
Fe = 0.58% (0.13 grams)
Cu = 56.4% (12.18 grams)
S = 20.03% (4.33 grams)

Solution Analysis: (Leach solution plus wash = 1000 ml)
Fe = 16.4 g/l (16.4 grams)
Cu = 0.46 g/l (0.46 grams)

Scrubber Solution Analysis:
S = 0.311 moles/l (9.97 grams)

Material Balances:
Feed = Residue + Solution + Scrubber Solution
Fe: 16.68 g = 0.13 + 16.4 = 16.53 g
Cu: 12.33 g = 12.18 + 0.46 = 12.64 g
S: 14.40 g = 4.33 + 9.97 = 14.30 g

After a few experiments it became evident that the progress of a leaching experiment could be followed simply by measuring the H_2S evolved. When H_2S evolution stopped or was very slow, the dissolution of iron was complete. The dissolution of copper continued, but at a slow rate compared to iron dissolution. Copper dissolution did not contribute significantly to the generation of H_2S. The rate of H_2S evolution was, therefore, a good measure of the rate of iron dissolution; it was not necessary to analyze the leach solution during the course of the experiment. It was only necessary to analyze the final leach solution for iron and copper (for material balance purposes).

In most of the leaching experiments, argon or helium was used as the purge gas. It was felt that this would prevent the oxidation, by air, of iron (II) in the leach solutions to iron (III). If iron (III) is present in the solution, it could increase the copper dissolution. The analytical data showed that in most runs the iron in solution was present as iron (II). An exact measure of the iron (III) was difficult because the iron (II) and total iron usually agreed within the precision of the analytical procedure. In some runs air was used as the cover gas. In these runs the iron (II) and total iron still were the same (within the analytical precision) and no increase in iron (III) was observed. In addition, no significant increase in copper dissolution was observed. Therefore, use of an inert cover gas during leaching does not appear to be necessary.

Concentrate Type

To determine how different concentrates would respond to acid leaching, the eight neutral-roasted concentrates were leached under identical conditions. The concentrates used had all been neutral-roasted in an inert atmosphere at 800°C for 16-24 hours.

The conditions used in the tests were not the optimum for leaching. Time did not permit determining the optimum leach condition for each neutral-roasted concentrate. Instead, it was necessary to select a standard set of (less than optimum) leach conditions for use in comparing the eight concentrates.

The procedure used was as follows. Fifty grams of neutral-roasted concentrate were placed in the reaction vessel and the vessel purged with argon. Three hundred ml of 4N hydrochloric acid (~100% excess) were added, and the system heated to the boiling point of the acid (~106°C). It took approximately 10 minutes for the acid to reach the boiling point. Each run lasted 90 minutes. H_2S evolution was essentially complete after 90 minutes with each concentrate.

The results obtained with the various concentrates are given in Table X. It is readily apparent from the data that since at least 67% of the sulfur in the original concentrate needs to be converted to H_2S that none of the neutral-roasted copper concentrates produced, under the leaching conditions used, the amount of H_2S needed for a workable process. The copper concentrates which are high in pyrite (Morenci and Tyrone) come the closest to meeting process requirements. The San Manuel, Pima and Anaconda concentrates, which are low in pyrite, produce the least H_2S. The Hecla concentrate (which is principally pyrite) after neutral-roasting reacted almost completely with the acid. The residue remaining after leaching contained only trace levels of iron and sulfur.

From the results presented, it is apparent that in order to obtain a workable process more H_2S must be produced from the copper concentrates. There are several ways in which this might be done.

1. Optimizing the leaching conditions.
2. Varying the neutral roasting conditions to change the composition of the neutral-roasted concentrates.
3. Add neutral-roasted pyrite to the neutral-roasted concentrate to increase the H_2S formation.

All three approaches were investigated using neutral-roasted Morenci, Pima and Anaconda concentrates.

In the laboratory studies the leach solution and solid residue were separated by filtrations using a #42 paper. In a commercial operation filtration would probably also be used for the separation. In the plant

TABLE X. Leaching Data for Neutral Roasted Concentrates

Reaction Conditions:

Temperature	-	∿ 106°C
Reaction Time	-	90 minutes
Concentrate	-	50.0 grams
Hydrochloric Acid	-	300 ml 4N acid

Neutral Roasted Concentrate*	Amount of Material in Concentrate Reacted, %***		
	Fe	Cu	S
Morenci	87.7	1.80	60.6
Pima	62.5	1.90	41.0
Anaconda	74.9	1.10	47.9
Tyrone	83.4	2.90	61.2
Lavender Pit	65.0	2.70	52.3
Battle Mountain	85.3	4.10	57.1
San Manuel	64.6	4.13	40.1
Hecla**	100.0		100.0

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* All concentrates neutral roasted at 800°C for 16-24 hours in helium or argon. See Table II for analyses.

** Only 25.0 grams of neutral roasted concentrate used.

*** Average of two or more runs: iron and copper dissolved in leach solution and sulfur evolved as H_2S.

the residue would have to be thoroughly washed to remove chloride effectively before further processing to recover the copper. The filtration characteristics of the leach residue are, therefore, an important factor to be considered. It was found that, with the exception of the neutral-roasted Pima, the leach residues were easily filtered and washed. Conflicting results were obtained with the Pima concentrate. In most runs the residue was as easy to filter and wash as the other concentrates. In a few runs, however, the residue was extremely difficult to filter. The cause of the filtration difficulties has not been identified.

Concentrate Composition

The composition of a neutral-roasted concentrate varies depending on the conditions of roasting. This variation in composition will in turn affect the results obtained during acid leaching. To determing how composition would affect the H_2S yield, samples of neutral-roasted Morenci, prepared under various conditions, were leached under identical conditions. The leach procedure was identical to that described in the previous section (fifty grams of neutral-roasted concentrate were leached in 300 ml of boiling $4\underline{N}$ HCl for 90 minutes).

The results obtained with neutral roasted Morenci concentrate are given in Table XI. The results show that the H_2S yield (and iron dissolution) is increased by increasing the metal-sulfur ratio of the neutral-roasted feed. This ratio is best increased by increasing the neutral-roasting temperature, lengthening the roasting time, or both. Maximum H_2S yield was obtained when the neutral-roasting temperature was high enough to melt the concentrate ($\sim$1000°C).

Differences in the mineralogical composition of concentrate roasted at different temperatures may also help explain the differences in the H_2S yield. Since the mineralogical composition of the neutral-roasted concentrate could not be adequately determined, however, it was impossible to evaluate this effect.

TABLE XI. Effect of Concentrate Composition on Leaching

Leaching Condition:

Concentrate - 50 g neutral roasted Morenci
Acid - 300 ml 4N HCl
Temperature - ~ 106°C
Reaction Time - 90 minutes

Composition of Neutral Roasted Concentrate:

Sample No.	Roasting Temperature	Composition, wt% Fe	Cu	S	M/S
1	800°C	32.3	23.7	29.2	$M_{1.05}S$
2	800°C	33.4	24.7	28.8	$M_{1.10}S$
3	970°C	37.3	28.5	30.5	$M_{1.17}S$
4	1005°C	33.5	25.9	25.2	$M_{1.23}S$

Results of Leaching Tests:

Sample No.	Amount of Material in Concentrate Reacted, %* Fe	Cu	S
1	75.9	2.9	52.3
2	87.7	1.8	60.6
3	88.6	0.97	62.2
4	95.6	4.0	71.1

---

* Fe and Cu dissolved in leach solution, S evolved as H_2S.

It was found that Morenci concentrate neutral-roasted at 1005°C was much more reactive than that produced at lower temperatures. Data presented in Figure 12 shows that the concentrate prepared at 1005°C reacts more rapidly with acid at room temperature than material prepared at 800°C does at 60 and 106°C. Another surprising factor is that the temperature of leaching has only a slight effect on the reaction rate for the material prepared at 1005°C.

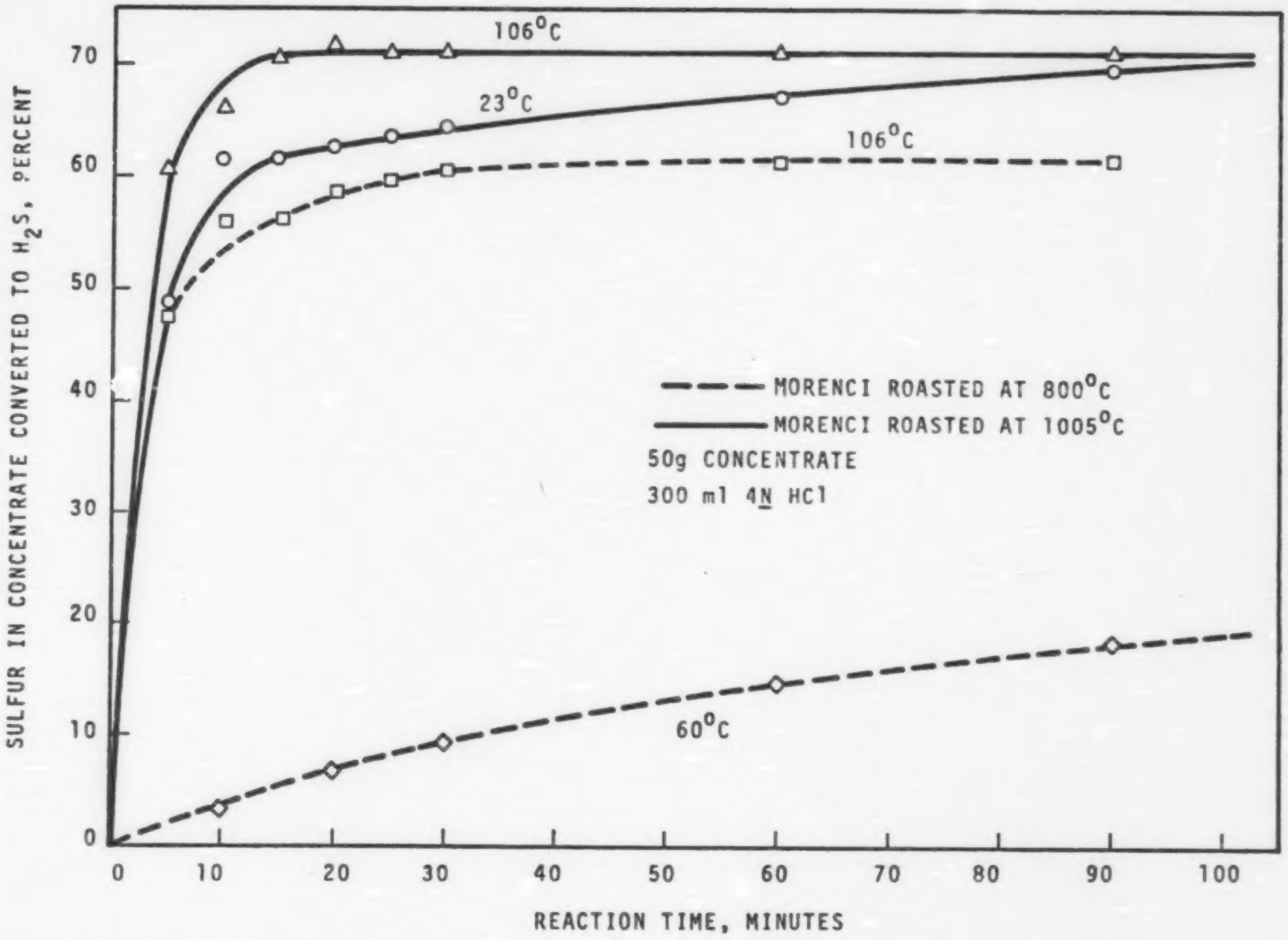

FIGURE 12. Reactivity of Neutral-Roasted Morenci Concentrate

Neutral-roasted Pima and Anaconda concentrates prepared at various temperatures were also leached to determine the effect of composition on H_2S generation and iron dissolution. Leaching conditions were identical for each experiment and were the same as those used with the Morenci concentrate. The results obtained are presented in Table XII. Again it was found that, in general, the higher the metal-sulfur ratio in the neutral-roasted concentrate (of a given type) the higher the H_2S yield and iron dissolution. Increased roasting temperature also increased the reactivity.

Copper dissolution during leaching of the various concentrates was erratic. In every run in which periodic samples were taken copper dissolution increased with time. However, there was considerable variation in the amount of copper dissolved in similar or duplicate runs. Reasons for the variability in copper dissolution have not been determined.

Tests with neutral-roasted Hecla pyrite showed the material dissolved almost completely in hydrochloric acid with essentially complete dissolution of the iron and conversion of sulfur to H_2S. One way of increasing the H_2S yield from neutral-roasted copper concentrates would be to leach a mixture of neutral-roasted pyrite and neutral-roasted copper concentrate (pyrite is usually available as a waste stream from the flotation plant in most copper operations). Roasting the pyrite and concentrate separately would insure sufficient H_2S production. A second possibility would be to combine the pyrite and concentrate prior to roasting. To see if this procedure could be used, mixtures of Hecla pyrite with Morenci, Pima and Anaconda concentrate were neutral-roasted in helium at 820-860°C for 16 hours and then leached. The results obtained are presented in Table XIII. The addition of pyrite to the Pima concentrate increases the H_2S yield on leaching to an acceptable level. With the Anaconda concentrate there was a small but significant increase in the H_2S yield. In the case of the Morenci, the H_2S yield decreased slightly but was within the reproducibility of the experimental procedure. One factor noted was that the reaction rate for neutral roasted concentrate-pyrite mixtures decreased compared to straight neutral

TABLE XII. Effect of Composition on Leaching of Neutral Roasted Pima and Anaconda Concentrates

Leaching Conditions:

50.0 g neutral roasted concentrate
300 ml 4N HCl
Temperature ~ 106°C
Reaction Time 90 minutes

Concentrate	Roasting Temp. °C	Comp. of Neutral Roasted Conc.				Amount of Material in Conc. Reacted, %*		
		wt% Fe	wt% Cu	wt% S	M/S	Fe	Cu	S
Pima	800	29.4	29.4	27.8	$M_{1.14}S$	62.5	1.90	41.0
Pima* A	860	29.1	30.9	25.5	$M_{1.25}S$	92.2	1.3	64.8
B	860	28.9	28.6	24.6	$M_{1.27}S$	86.3	0.6	56.3
Pima	970	28.9	29.7	24.7	$M_{1.28}S$	88.2	0.6	59.6
Pima	1005	29.1	29.3	24.8	$M_{1.27}S$	92.4	1.6	59.7
Anaconda	800	23.2	34.9	26.5	$M_{1.17}S$	74.9	1.1	47.9
Anaconda	1000	28.1	42.3	26.9	$M_{1.39}S$	85.6	4.8	51.8

---

* Fe and Cu dissolved in leach solution and S evolved as H_2S.

TABLE XIII. Leaching of Neutral Roasted Pyrite-Copper Concentrate Mixtures

Leaching Conditions:

50.0 g neutral roasted concentrate
400 ml 4N HCl
Temperature ~ 106°C
Reaction time up to 120 minutes

Leaching Results:

Feed to Roaster	Roasting Temp. (°C)	Roasting Time (hrs)	Comp. of Neutral Roasted Conc., wt%			Amount Reacted in Leaching, %*		
			Fe	Cu	S	Fe	Cu	S
80% Morenci-20% Pyrite	860	16	35.4	21.1	28.2	84.2	1.1	59.3
57.5% Pima-42.5% Pyrite	820	16	39.5	30.0	28.8	79.1	2.5	68.0
50% Anaconda-50% Pyrite	860	16	35.0	20.5	28.0	71.4	2.8	54.1

---

* Fe and Cu dissolved in leach solution and S evolved as H_2S.

roasted concentrates. Normally at 106°C the leaching reaction was essentially complete in 60 minutes or less. With the neutral-roasted mixtures it required 90-120 minutes for completion.

Based on the results of the leach tests with concentrate-pyrite mixtures, it appears that separate roasting of the concentrates and pyrite would be preferred to combined roasting.

Samples of Morenci concentrate which had been roasted at 800°C in He-2% O_2 were leached in 4N HCl at 106°C. The H_2S yield was greatly decreased as was the iron dissolution. The maximum H_2S yield obtained was only 35%. In addition the reaction rate was greatly decreased. It required approximately 10 hours before the evolution of H_2S stopped. Iron dissolution was less than 60% and copper dissolution less than 1%. These results are difficult to explain. If oxidation of the samples occurred during roasting, the iron dissolution should be much higher. Similarly if sulfation occurred during roasting, both iron and copper dissolution should be higher. The only conclusion that can be made is that the presence of oxygen in the cover gas during roasting can adversely affect the process by reducing the H_2S yield obtained on roasting.

When samples roasted in Ar - 4% H_2 were leached, the yields obtained were similar to those obtained with concentrate roasted in argon. Therefore the use of a reducing atmosphere during roasting does not appear to adversely affect the process.

Operating Variables

The principal operating variables which affect the leaching reaction are:

1. acid concentration,
2. acid-concentrate ratio,
3. reaction temperature.

The effect of each variable on the leaching of roasted Morenci, Pima, and Anaconda concentrates was studied. The concentrates used were all neutral roasted at 800°C in flowing argon for 24 hours (see Table II for analyses).

It was found that the acid concentration used had a significant effect on the leaching of neutral roasted Morenci concentrate (the maximum acid concentration tested was that of the azeotrope ~6M). Maximum iron dissolution and H_2S formation was obtained with an initial acid concentration of 3-4 molar (see Figure 13). A 100% excess of acid (based on iron content of the feed) was used in each run. Both iron dissolution and H_2S production dropped sharply as the initial acid concentration was varied from the optimum. The dissolution of copper increased rapidly with increasing acid concentration and was especially severe when the initial acid concentration was greater than 4M. The amount of undissolved solid residue from the leaching reaction varied with acid concentration and was a minimum, as expected, when H_2S production and iron dissolution were a maximum (see Figure 14).

The initial acid concentration has far less effect on the leaching of neutral-roasted Pima concentrate as far as H_2S production and iron dissolution is concerned (see Figure 15). Both H_2S formation and iron dissolution increased slightly with increased acid concentration. As was the case with Morenci concentrate, copper dissolution increased rapidly with increasing acid concentration.

With neutral-roasted Anaconda concentrate maximum iron dissolution and H_2S production were obtained with an initial acid concentration of about 4M (see Figure 16). Changes from the optimum initial acid concentration caused only a slight decrease in H_2S formation. Copper dissolution increased with increasing acid concentration but not to the same degree as with Morenci and Pima concentrates.

The ratio of acid to concentrate used can affect the H_2S yield obtained. With neutral-roasted Morenci, a 100% excess of acid (in excess of that needed to react with the iron in the feed) was required to obtain the maximum H_2S yield and iron dissolution (see Figure 17). With neutral roasted Pima, H_2S formation and iron dissolution were relatively independent of the excess acid used (see Figure 18). The neutral-roasted Anaconda concentrate gave a slight increase in H_2S production with increasing acid-concentrate ratio.

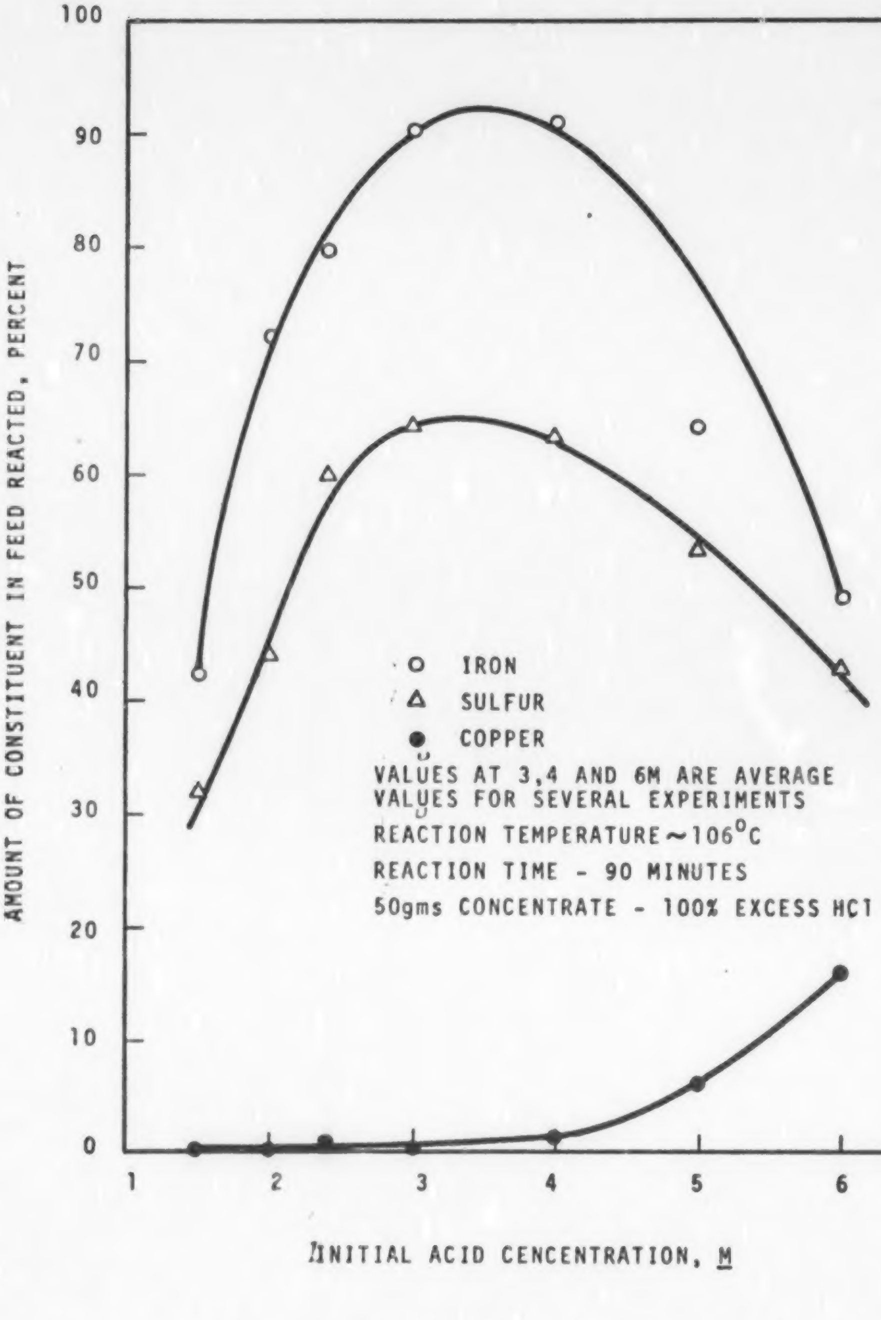

FIGURE 13. Effect of Initial Acid Concentration on Leaching of Neutral-Roasted Morenci Concentrate

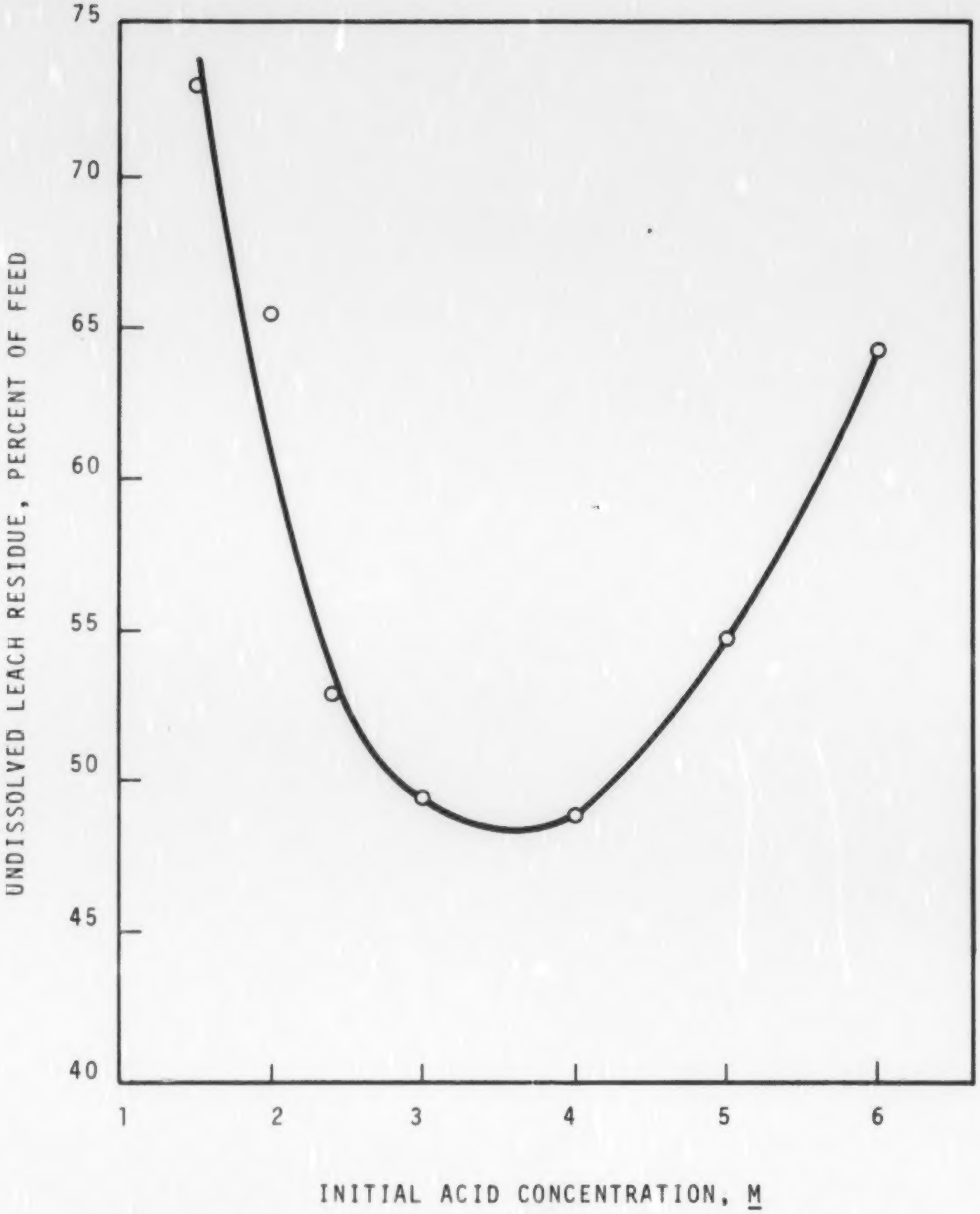

FIGURE 14. Effect of Initial Acid Concentration on Dissolution of Neutral-Roasted Morenci Concentrate

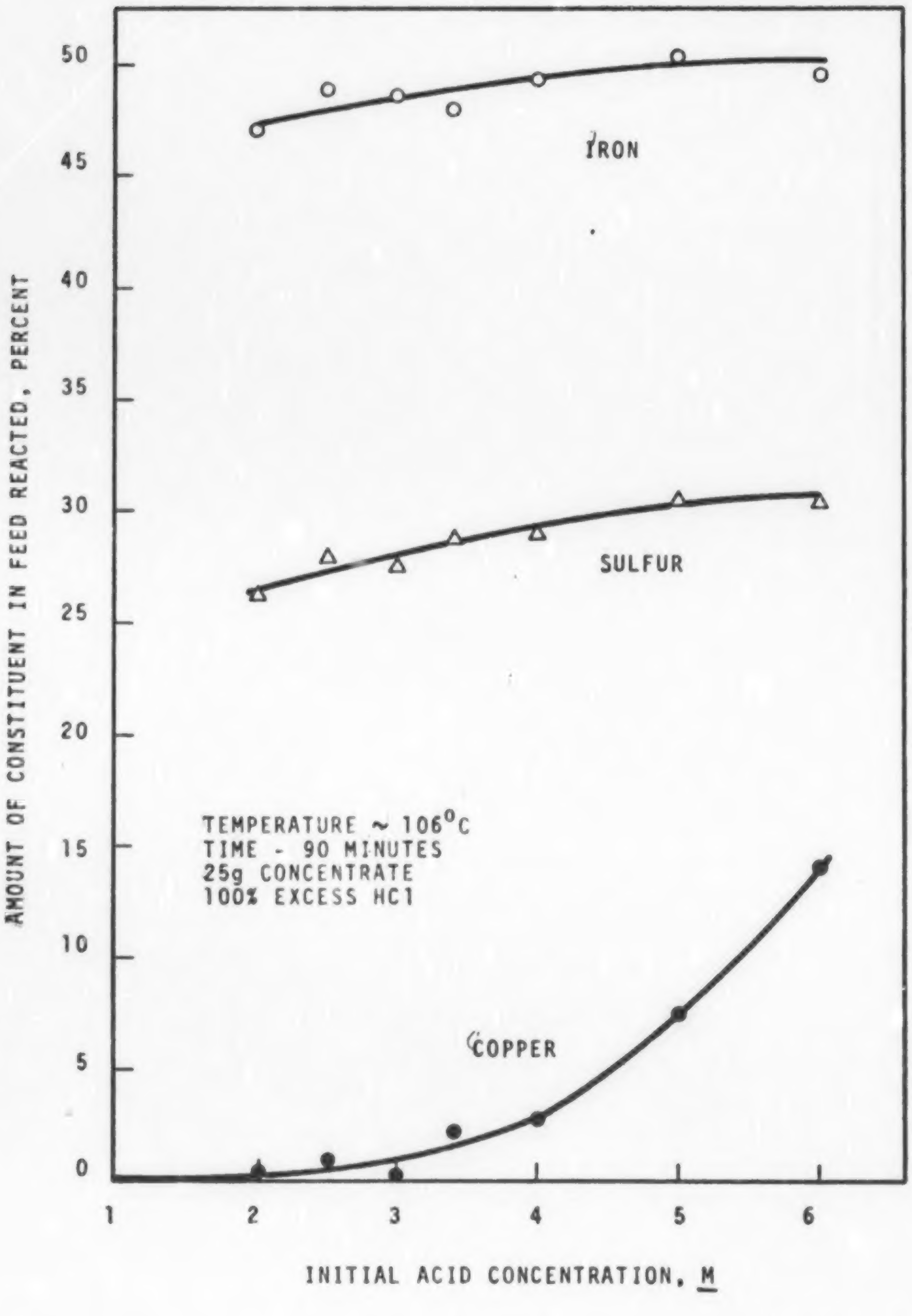

FIGURE 15. Effect of Initial Acid Concentration on Leaching of Neutral Roasted Pima Concentrate

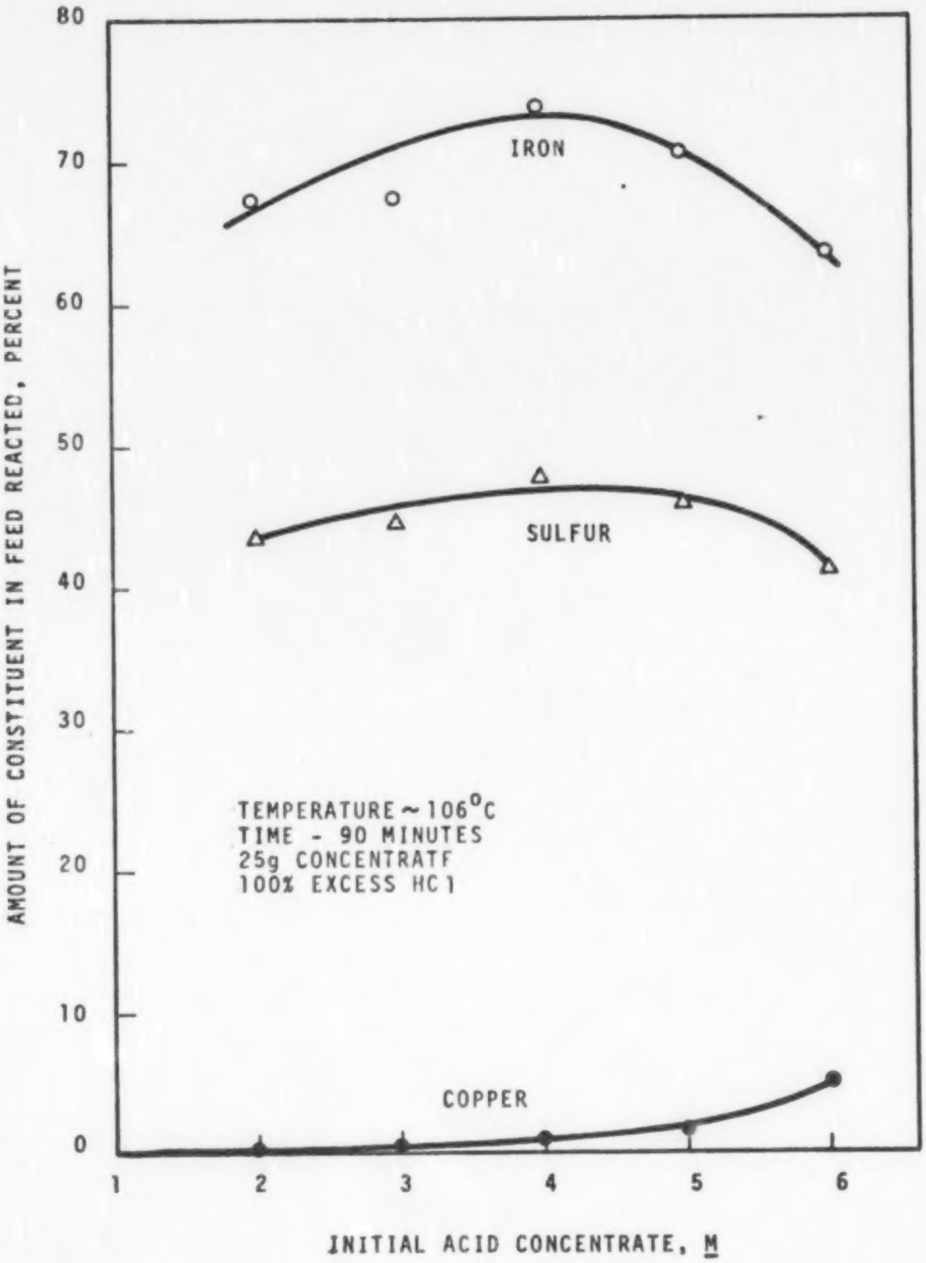

FIGURE 16. Effect of Initial Acid Concentration on the Leaching of Neutral-Roasted Anaconda Concentrate

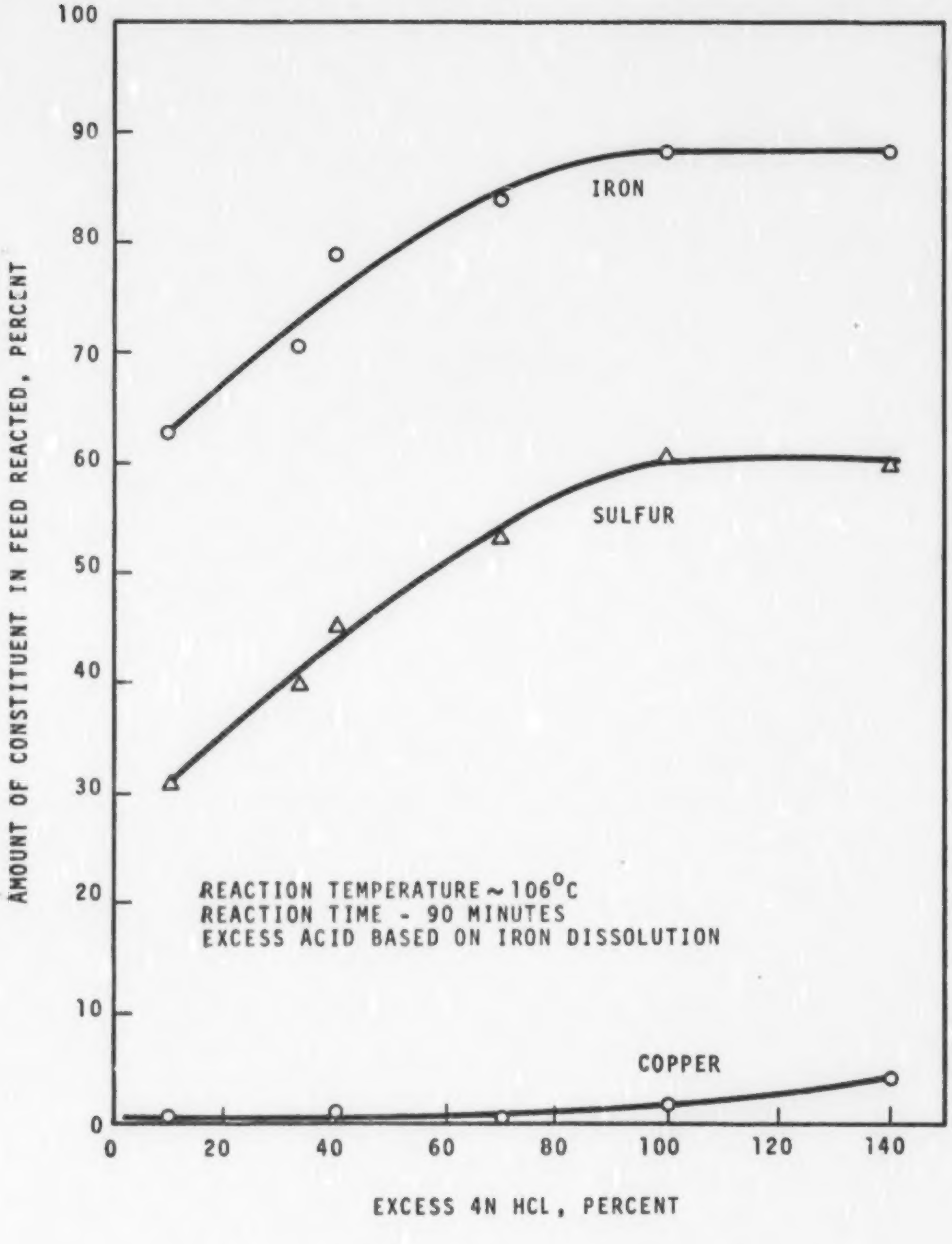

FIGURE 17. Effect of Excess Acid on Leaching of Neutral-Roasted Morenci Concentrate

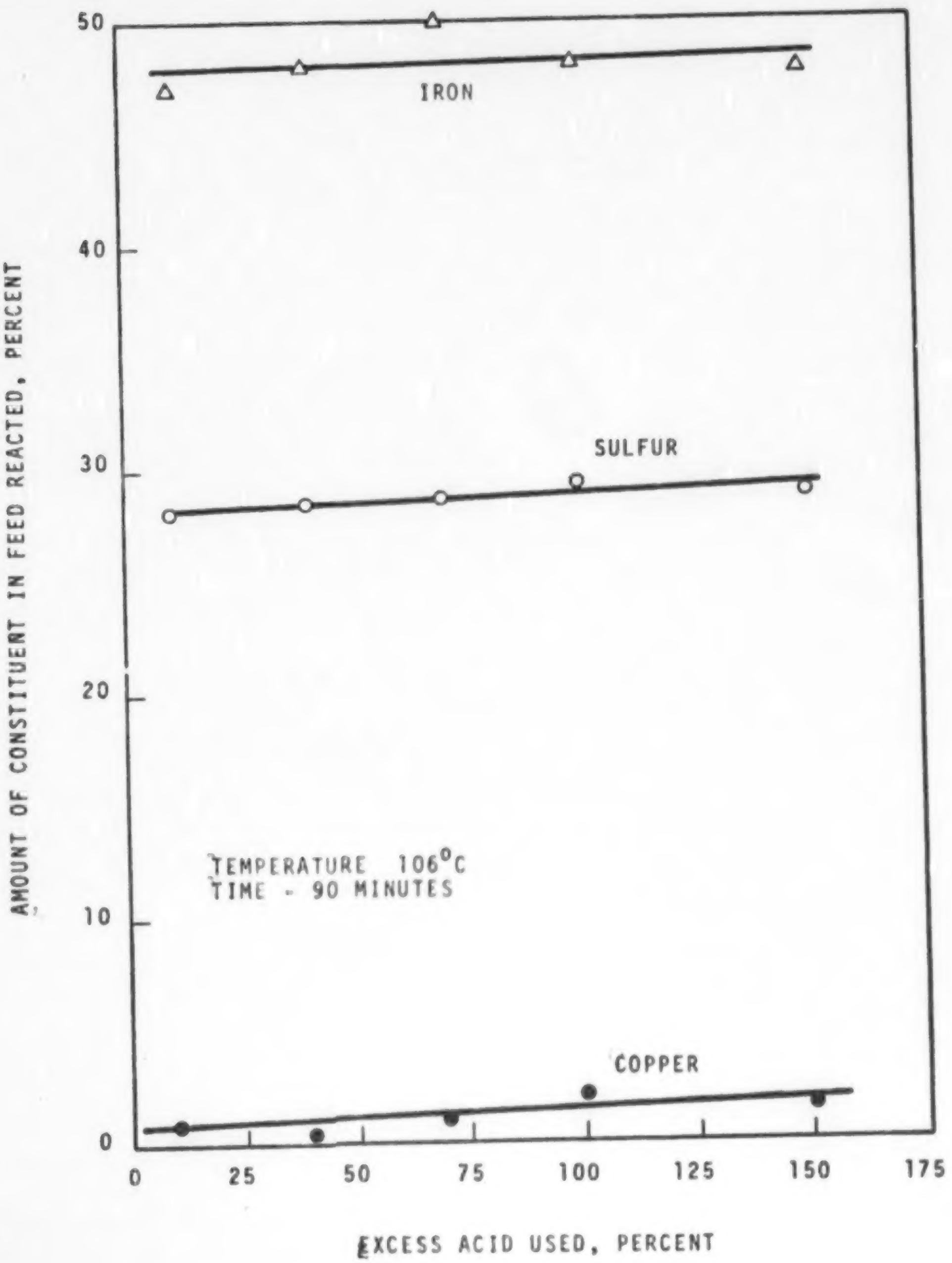

FIGURE 18. Effect of Excess Acid on Leaching of Neutral-Roasted Pima Concentrate

The reaction temperature has a significant effect on the leaching reaction. The effect observed was unexpected in that maximum H_2S production and iron dissolution were obtained at temperatures below the boiling point of the acid solution. The results obtained with the three concentrates are shown in Figures 19-21. The tests were carried out by bringing the 4N HCl to the reaction temperature and then adding the concentrate. The runs were continued until the evolution of H_2S was essentially complete. Maximum H_2S production was obtained with each concentrate when the reaction temperature was between 80-90°C.

With neutral roasted Morenci the rate of H_2S formation increases with increasing reaction temperature as shown in Figure 22. At a temperature of 106°C, H_2S formation and iron dissolution is complete in 30 minutes or less. At 70°C and below the reaction rate decreases rapidly and reaction times of 4 hours or longer are required. At 80°C, where maximum H_2S formation is obtained (with Morenci), the reaction is complete in about 60-70 minutes. The reactivity of neutral-roasted Anaconda is similar to that of the neutral-roasted Morenci, while reactivity of the neutral-roasted Pima was somewhat less. With each concentrate maximum H_2S yield is obtained at a reduced reaction temperature at the expense of increased reaction time.

One additional factor was noted with regard to reaction temperature. If the acid and concentrate were combined and heated to the reaction temperature, the H_2S yield was higher than when the concentrate was added to the acid at the reaction temperature. This was especially true at reaction temperatures of 90°C and above. The reason for this phenomenon has not been resolved.

Fate of Impurities During Leaching

Samples of solution and residue from a leaching experiment with neutral roasted Anaconda concentrate were analyzed to determine the fate of impurities during leaching. Table XIV shows how the impurities divide between the leach solution and solid residue. Data for the original concentrate and neutral-roasted concentrate are also shown (to put the data on a uniform

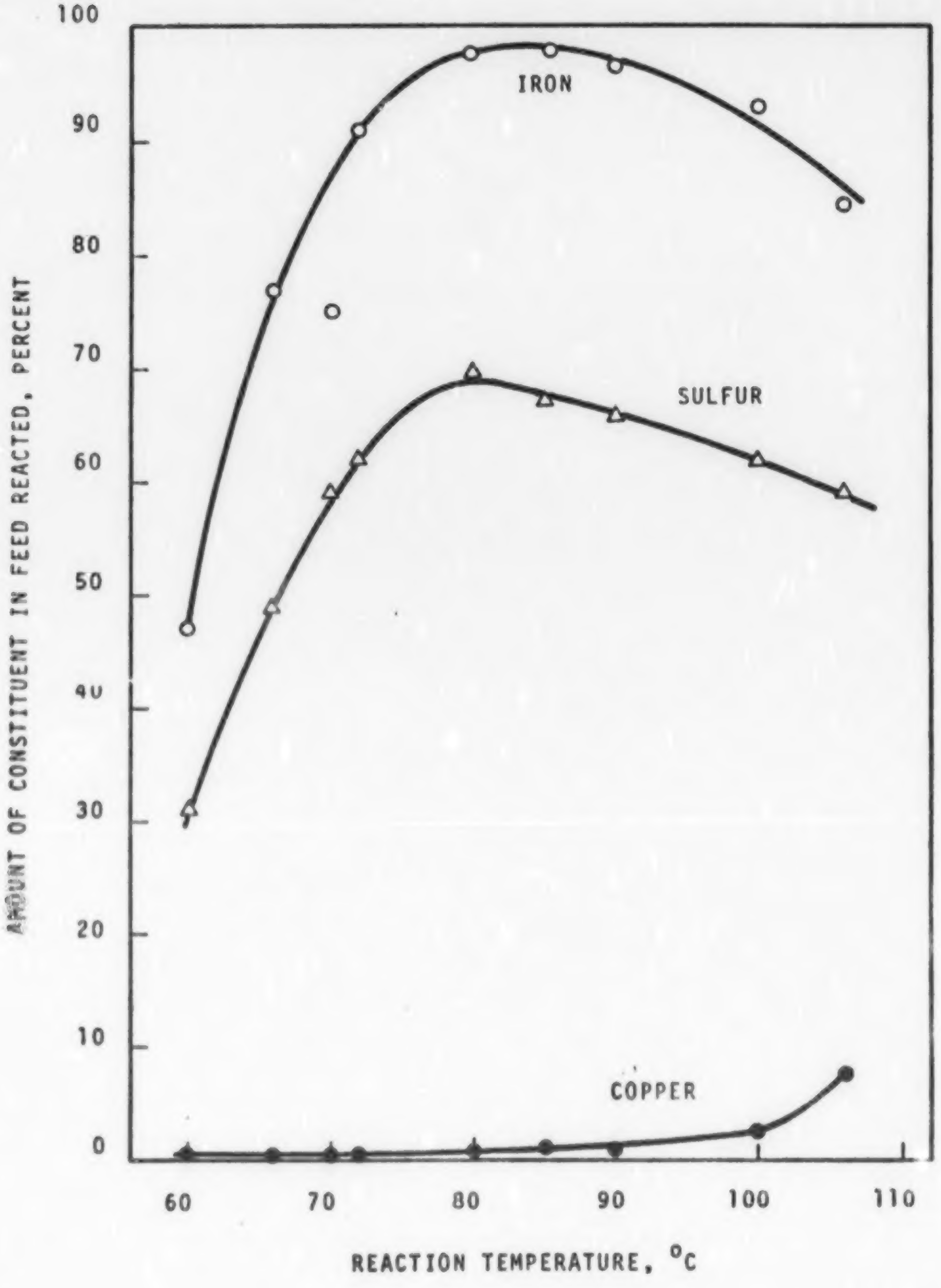

FIGURE 19. Effect of Temperature on Leaching of Neutral-Roasted Morenci Concentrate

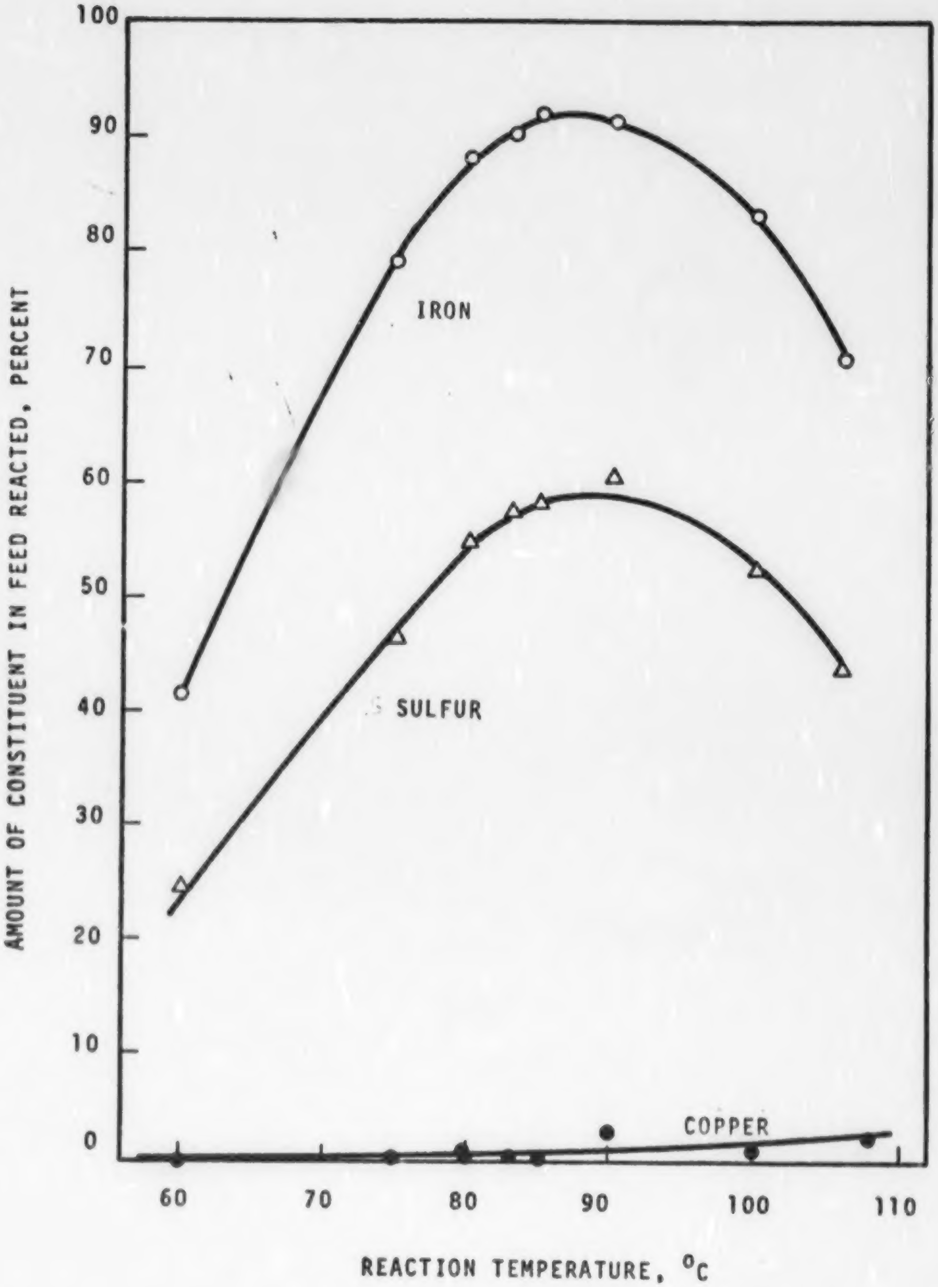

FIGURE 20. Effect of Temperature on Leaching of Neutral-Roasted Pima Concentrate

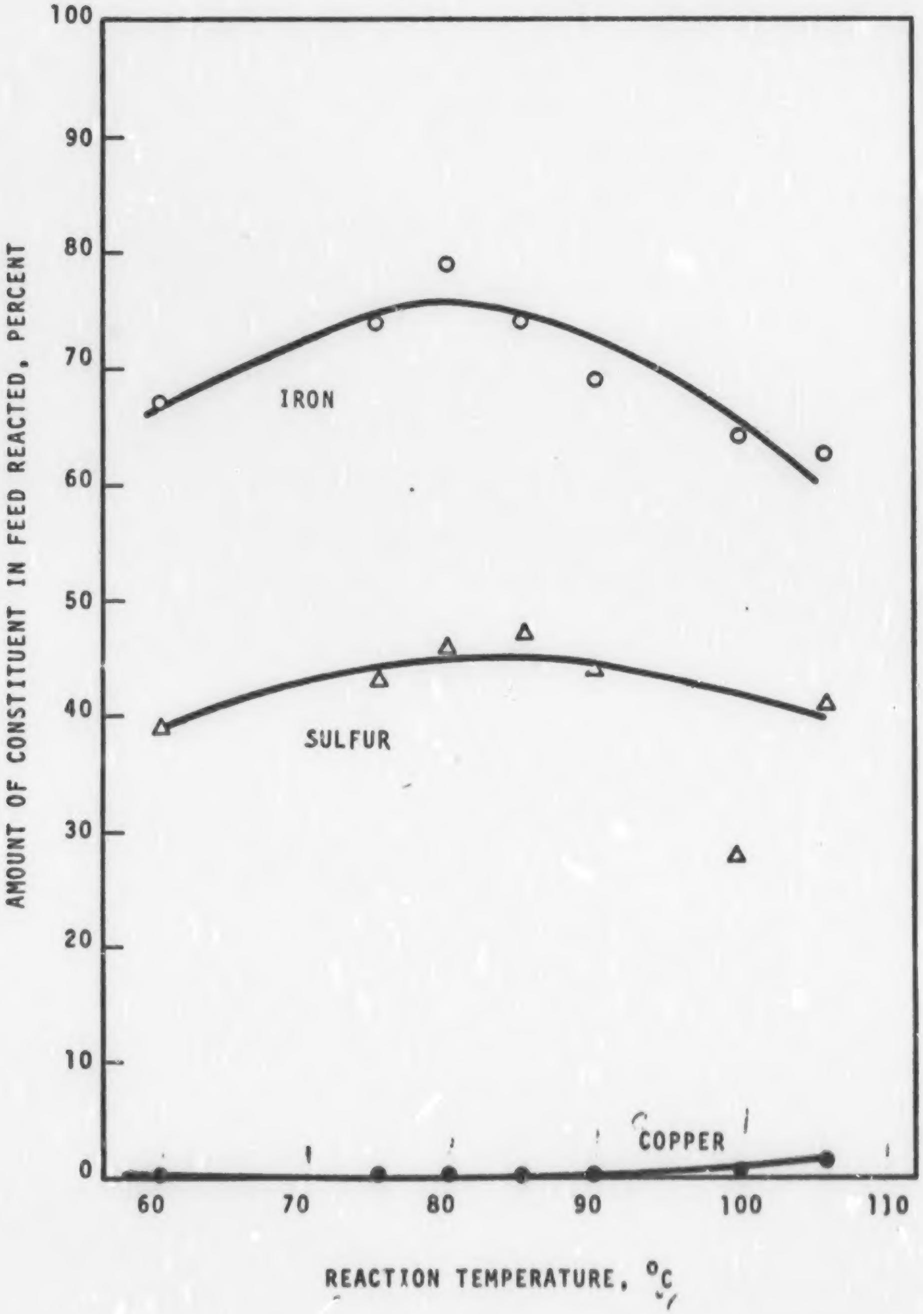

FIGURE 21. Effect of Temperature on Leaching of Neutral-Roasted Anaconda Concentrate

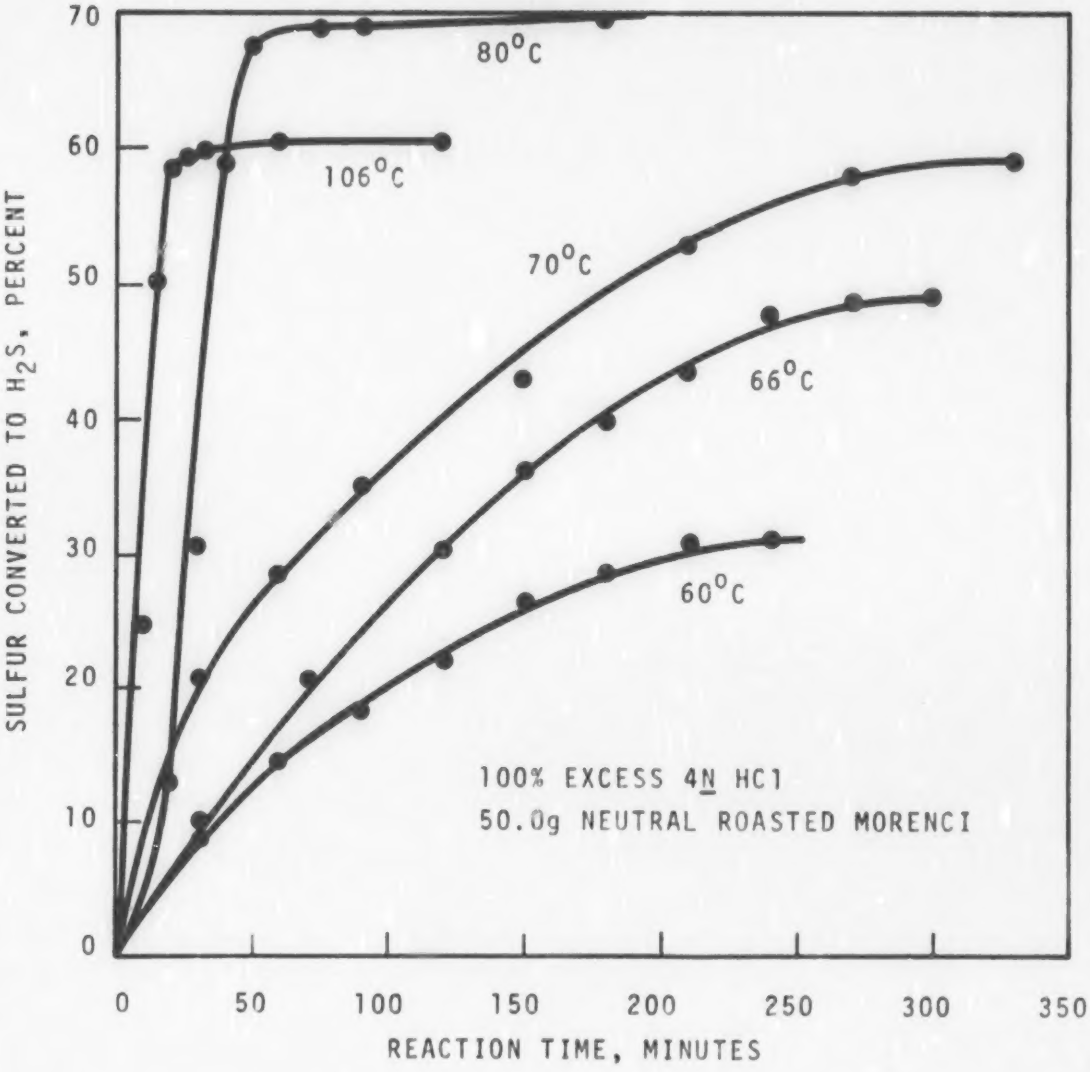

FIGURE 22. Effect of Reaction Temperature on the Leaching of Neutral-Roasted Morenci Concentrate

TABLE XIV. Fate of Impurities During Leaching of Anaconda Concentrate

Impurity	Grams Per 100 Grams of Original Concentrate			
	Concentrate	Neutral Roasted Concentrate	Leach Residue	Leach Solution
As	1.86	0.17	0.074	0.084
Sb	0.037	0.06	0.05	0.10
Zn	6.2	3.76	0.20	3.12
Pb	0.05	0.20	0.20	0.32
Mo	0.05	0.064	0.005	0.005
Bi	0.03	0.032	0.006	0.008
Cd	0.12	0.50	0.0025	0.0016
Se	0.029	0.016	0.0094	0.0064
Te	0.025	0.0051	0.0035	0.0024
Hg	0.024	0.00016	0.0002	0.000016
Ag*	10.42	10.2	2.24	7.70
Au*	0.07	0.051	0.06	0.012

---

*In troy ounces per ton of original concentrate.

basis the impurity levels are reported as grams per 100 grams of original concentrate). The overall material balances for the trace level impurities are poor due to analytical problems. It is apparent, however, that the trace impurities divide between the leach solution and the solid residue. The bulk of the zinc ends up in the leach solution as does the silver, while the bulk of the gold remains in the residue.

When the leach solution is treated with H_2S most of the copper precipitates as does the silver and whatever gold is present (see Table XV). The effect on the other impurities in the leach solution is minimal.

TABLE XV. Effect H_2S Treatment on Impurities in the Leach Solution

Impurity	Concentration, g/l Original Leach Solution	 Treated Leach Solution
Cu	0.92	0.05
As	0.105	0.06
Sb	0.125	0.10
Zn	3.90	4.20
Pb	0.40	0.40
Mo	0.006	0.005
Bi	0.010	0.002
Cd	0.002	0.008
Se	0.008	0.009
Te	0.003	0.002
Hg	0.00002	0.00001
Ag	0.033	0.002
Au	0.00005	Trace

Process Optimization

The laboratory studies have shown that it will be possible to achieve sufficient H_2S production with most types of copper concentrates to make the proposed process viable. It will require, however, optimization of the neutral-roasting and acid leaching operations and pyrite addition to insure adequate H_2S production from low iron concentrates.

To maximize H_2S production with all types of concentrates, the following process conditions should be met.

1. The neutral roasting operation should be carried out at the highest temperature possible ($\geq$800°C). Melting of the concentrate during roasting produces the optimum product from a reactivity and H_2S generation standpoint.

2. Care must be taken to exclude oxygen from the cover gas during roasting. A neutral or reducing atmosphere must be used to obtain maximum H_2S production upon leaching.
3. If possible, a mixture of neutral-roasted copper concentrate and neutral-roasted pyrite should be used for leaching. This will insure adequate H_2S production. Since a typically sized copper smelter would require more than one roaster, the copper concentrate and pyrite can and should be roasted separately.
4. The leaching should be carried out with an initial acid concentration of about 4$\underline{N}$ at a temperature of 80-90°C. An excess of acid should be used. The excess required will depend on the concentrate but will probably be at least 50% and possibly as much as 100%.
5. The residence time of the concentrate in the leach tank should be the shortest possible time consistent with the required H_2S production. Increasing the residence time will increase copper dissolution.

If the process operation conforms to the conditions set forth above, the H_2S production will be sufficient for a viable process.

ECONOMIC ANALYSIS OF PROCESS

The cost of utilizing the proposed process for a 300 tons per day copper smelting operation was estimated based on the data developed in the laboratory studies. Two estimates were prepared: one assumed the use of a chalcocite (Morenci) concentrate feed and the second a chalcopyrite (Pima) concentrate feed. In each case pyrite addition was used to increase the availability of H_2S. The pyrite concentrate was assumed to be available as a by-product stream from the flotation mill. There may be some question concerning the real need for additional pyrite for Morenci concentrate processing, however pyrite addition is required with the Pima concentrate. It was used in the Morenci case simply to insure adequate H_2S formation. The pyrite would be roasted separately from the copper concentrate, and combined with the neutral roasted copper concentrate prior to leaching.

The following assumptions were also made in making the cost estimates:

1. The copper-bearing residue from the leaching operation would be fed directly to a converter. This eliminates the need for a reverberatory furnace.
2. HCl recovery and conversion of ferrous chloride to ferric oxide would be carried out in equipment similar to that currently being used to process hydrochloric acid pickle liquor(4) in the steel industry.
3. The reaction of H_2S and SO_2 to form elemental sulfur would be carried out using the "citrate" process developed by the U.S. Bureau of Mines.(36) If some SO_2 release could be tolerated, a modified Claus process could be used for the reaction at a somewhat lower cost.
4. The precious metals in the concentrates would end up in the blister copper from the converter. They would be recovered when the copper is refined by electrolysis.
5. The impurities in the concentrate, other than the precious metals, were ignored in preparing the cost estimates.

Process flow diagrams were prepared for the two cases under consideration and are shown in Figures 23 and 24. Stream flows were calculated using the data developed in the laboratory studies. The bases used in the calculations are shown in Table XVI. Impurities in the concentrates were not considered in the preparation of the flow diagrams.

For the purpose of the cost estimates, the overall smelter process was broken down into five major operations. Capital and operating costs for each major operation were estimated separately (the various subsidiary operations were included in the first estimates for the principal operations). The five major operations are:

1. Neutral Roasting System - This includes storage, drying and neutral roasting of the concentrates; particulate removal from the roaster off-gas; condensation, collection and stockpiling of the elemental sulfur; and quenching and granulation of the neutral roasted concentrates.
2. Acid Leaching System - This operation includes blending of the neutral roasted concentrates; leaching of the concentrates; filtration of the leach slurry and washing of the solid residue; treatment of the leach solution with H_2S to precipitate the dissolved copper and precious metals; filtration of the leach solution to collect the precipitated copper and precious metals; washing of the precipitate; and collection of the H_2S from the leach circuit.
3. Acid Recovery System - This includes evaporation of the filtered leach solution to remove the excess water; conversion of the ferrous chloride to ferric oxide and hydrogen chloride; collection of the hydrogen chloride as 4 to 5N hydrochloric acid; and handling and stockpiling of the ferric oxide.
4. Sulfur Dioxide Collection and Sulfur Production - This operation includes collection of the SO_2-containing gases from the converter; handling of the hydrogen sulfide gas stream; reaction of the SO_2 and H_2S in an aqueous citrate system to form elemental sulfur; stockpiling of the sulfur; and stack-venting of the SO_2-bearing off-gas (approximately 0.4% of the sulfur in the total plant feed ends up in the stack gas from the SO_2 recovery unit).

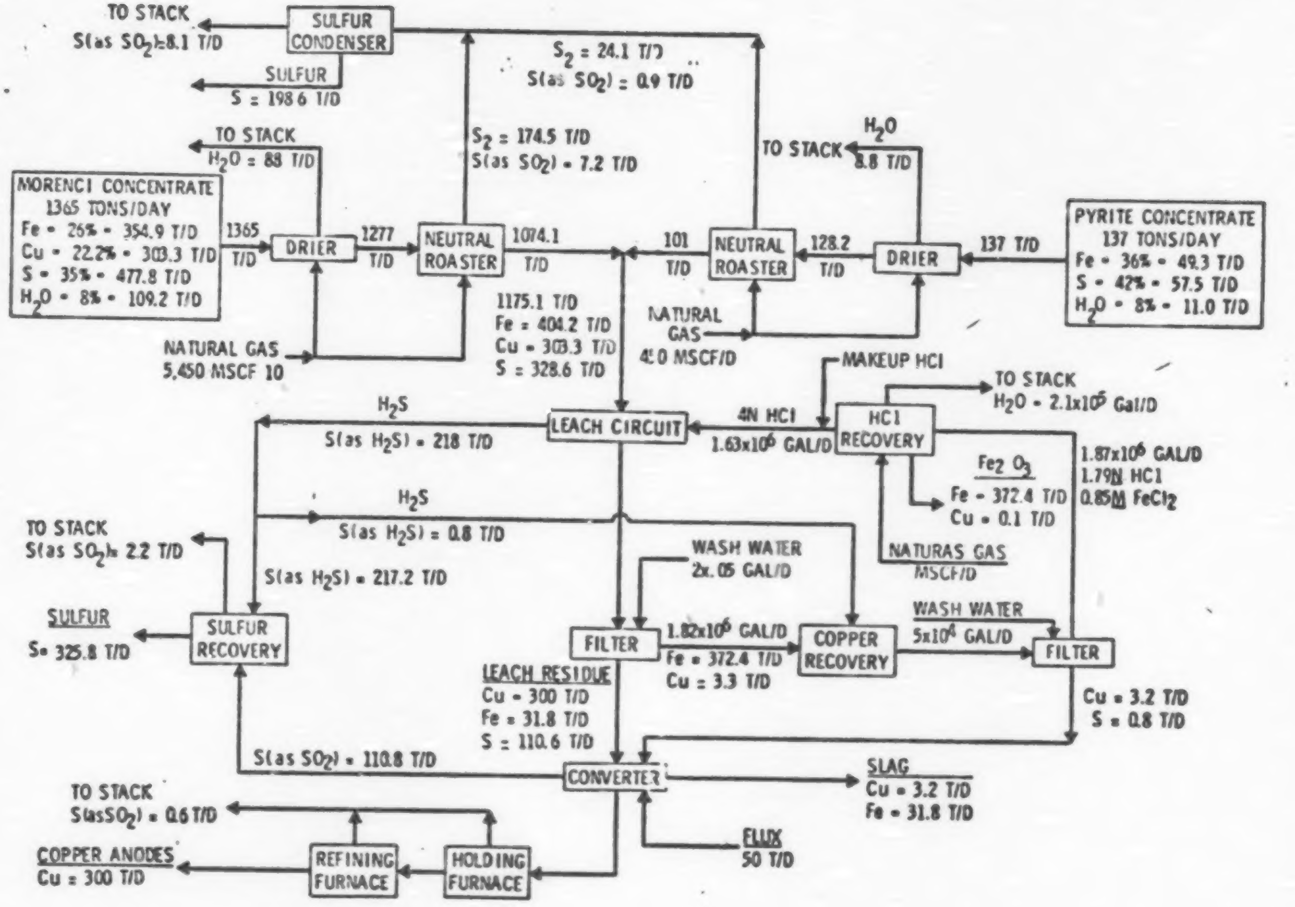
TO STACK
S(as SO2)=8.1 T/D
SULFUR CONDENSER
SULFUR
S = 198.6 T/D
S2 = 24.1 T/D
S(as SO2) = 0.9 T/D
TO STACK
H2O = 88 T/D
S2 = 174.5 T/D
S(as SO2) = 7.2 T/D
TO STACK
H2O
8.8 T/D
MORENCI CONCENTRATE
1365 TONS/DAY
Fe = 26% = 354.9 T/D
Cu = 22.2% = 303.3 T/D
S = 35% = 477.8 T/D
H2O = 8% = 109.2 T/D
1365 T/D
DRIER
1277 T/D
NEUTRAL ROASTER
1074.1 T/D
101 T/D
NEUTRAL ROASTER
128.2 T/D
DRIER
137 T/D
PYRITE CONCENTRATE
137 TONS/DAY
Fe = 36% = 49.3 T/D
S = 42% = 57.5 T/D
H2O = 8% = 11.0 T/D
NATURAL GAS
5,450 MSCF 10
1175.1 T/D
Fe = 404.2 T/D
Cu = 303.3 T/D
S = 328.6 T/D
NATURAL GAS
4.0 MSCF/D
MAKEUP HCl
TO STACK
H2O = 2.1x10^6 Gal/D
H2S
S(as H2S) = 218 T/D
LEACH CIRCUIT
4N HCl
1.63x10^6 GAL/D
HCl RECOVERY
1.87x10^6 GAL/D
1.79N HCl
0.85M FeCl2
Fe2 O3
Fe = 372.4 T/D
Cu = 0.1 T/D
H2S
S(as H2S) = 0.8 T/D
NATURAS GAS
MSCF/D
TO STACK
S(as SO2) = 2.2 T/D
WASH WATER
2x.05 GAL/D
S(as H2S) = 217.2 T/D
WASH WATER
5x10^4 GAL/D
SULFUR
S = 325.8 T/D
SULFUR RECOVERY
FILTER
1.82x10^6 GAL/D
Fe = 372.4 T/D
Cu = 3.3 T/D
COPPER RECOVERY
FILTER
LEACH RESIDUE
Cu = 300 T/D
Fe = 31.8 T/D
S = 110.6 T/D
Cu = 3.2 T/D
S = 0.8 T/D
S(as SO2) = 110.8 T/D
CONVERTER
SLAG
Cu = 3.2 T/D
Fe = 31.8 T/D
TO STACK
S(as SO2) = 0.6 T/D
COPPER ANODES
Cu = 300 T/D
REFINING FURNACE
HOLDING FURNACE
FLUX
50 T/D

FIGURE 23. Process Flow Diagram for 300 T/D Copper Smelter Using Morenci Concentrate Plus Pyrite Concentrate

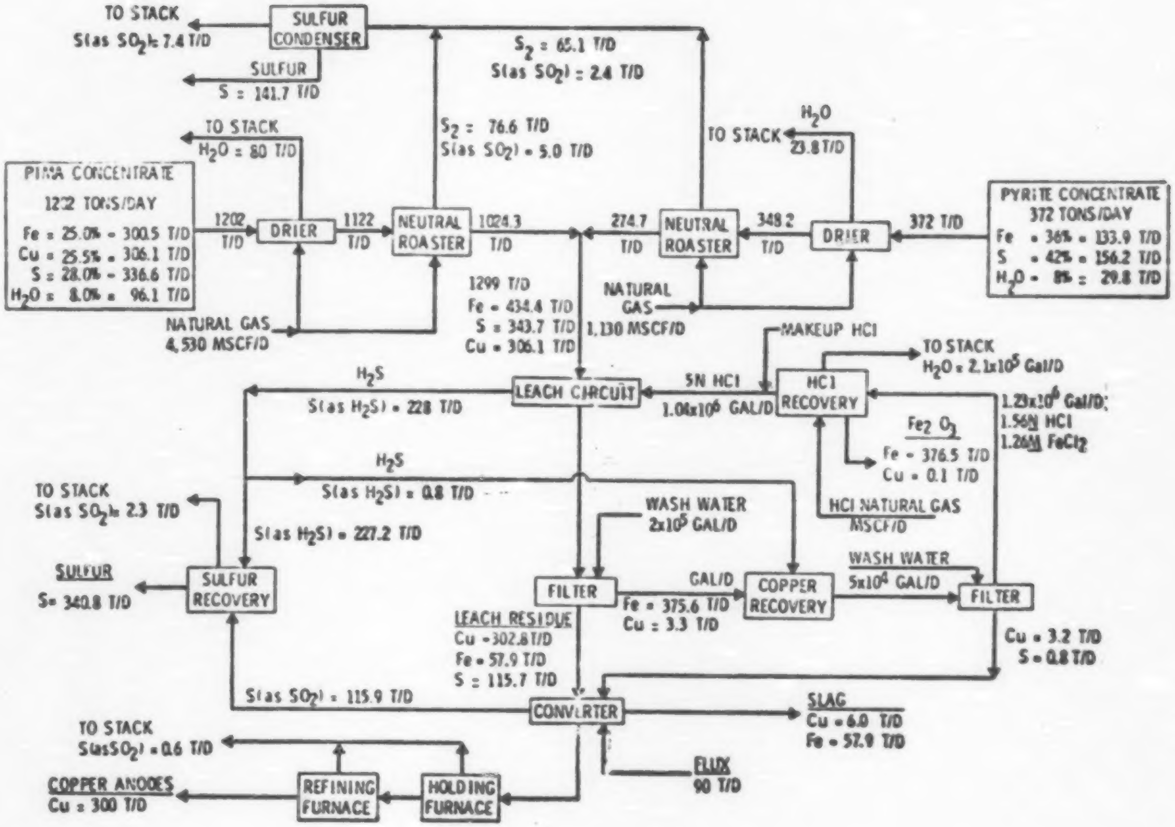
TO STACK
S(as SO_2) = 7.4 T/D
SULFUR CONDENSER
SULFUR
S = 141.7 T/D
S_2 = 65.1 T/D
S(as SO_2) = 2.4 T/D
TO STACK
H_2O = 80 T/D
S_2 = 76.6 T/D
S(as SO_2) = 5.0 T/D
TO STACK
H_2O
23.8 T/D
PIMA CONCENTRATE
1222 TONS/DAY
Fe = 25.0% = 300.5 T/D
Cu = 25.5% = 306.1 T/D
S = 28.0% = 336.6 T/D
H_2O = 8.0% = 96.1 T/D
1202 T/D
DRIER
1122 T/D
NEUTRAL ROASTER
1024.3 T/D
274.7 T/D
NEUTRAL ROASTER
348.2 T/D
DRIER
372 T/D
PYRITE CONCENTRATE
372 TONS/DAY
Fe = 36% = 133.9 T/D
S = 42% = 156.2 T/D
H_2O = 8% = 29.8 T/D
NATURAL GAS
4,530 MSCF/D
1299 T/D
Fe = 434.4 T/D
S = 343.7 T/D
Cu = 306.1 T/D
NATURAL GAS
1,130 MSCF/D
MAKEUP HCl
TO STACK
H_2O = 2.1x10^5 Gal/D
H_2S
S(as H_2S) = 228 T/D
LEACH CIRCUIT
5N HCl
1.04x10^6 GAL/D
HCl RECOVERY
1.23x10^6 Gal/D;
1.56N HCl
1.26M $FeCl_2$
Fe_2O_3
Fe = 376.5 T/D
Cu = 0.1 T/D
H_2S
S(as H_2S) = 0.8 T/D
HCl NATURAL GAS
MSCF/D
TO STACK
S(as SO_2) = 2.3 T/D
S(as H_2S) = 227.2 T/D
WASH WATER
2x10^5 GAL/D
WASH WATER
5x10^4 GAL/D
SULFUR
S = 340.8 T/D
SULFUR RECOVERY
FILTER
GAL/D
Fe = 375.6 T/D
Cu = 3.3 T/D
COPPER RECOVERY
FILTER
Cu = 3.2 T/D
S = 0.8 T/D
LEACH RESIDUE
Cu = 302.8 T/D
Fe = 57.9 T/D
S = 115.7 T/D
S(as SO_2) = 115.9 T/D
CONVERTER
SLAG
Cu = 6.0 T/D
Fe = 57.9 T/D
TO STACK
S(as SO_2) = 0.6 T/D
FLUX
90 T/D
COPPER ANODES
Cu = 300 T/D
REFINING FURNACE
HOLDING FURNACE

FIGURE 24. Process Flow Diagram for a 300 T/D Copper Smelter Using Pima Concentrate Plus Pyrite Concentrate

TABLE XVI. Bases Used in Preparing Flow Diagrams

		Morenci Smelter	Pima Smelter
1.	Copper Production (tons/day)	300	300
2.	Feed-Concentrate (tons/day)	1365	1202
3.	Feed-Pyrite (tons/day	207	429
4.	Drier Temperature (°C)	200	200
5.	Concentrate Roaster Temperature (°C)	900	900
6.	Pyrite Roaster Temperature (°C)	800	800
7.	S in Concentrate Converted to SO_2 in Roaster (%)	1.5	1.5
8.	S in Pyrite Converted to SO_2 in Roaster (%)	1.6	1.6
9.	Leach Acid Concentration (N)	4	5
10.	Excess Acid Used (%)	88	40
11.	S in Neutral Roasted Concentrate Converted to H_2S (%)	62.6	55
12.	S in Neutral Roasted Pyrite Converted to H_2S (%)	100	100
13.	SO_2 Conversion to Elemental Sulfur (%)	98	98
14.	S Content of Blister Copper (wt%)	0.2	0.2

5. Converter Operation - This includes operation of the converter to form blister copper, fire refining of the blister copper, casting into anodes, handling and disposal of the converter slag, collection of the SO_2-bearing gases, cooling and cleaning of the gases in a cyclone and waste heat boiler.

The products from the process are copper anodes containing the precious metals; ferric oxide of fairly high purity; pure elemental sulfur from the SO_2 recovery unit; and impure elemental sulfur from the neutral roasters.

If the elemental sulfur is to be marketed, the sulfur from the neutral roasters would require additional purification. Add-on equipment could be used for the purification at a nominal cost. The ferric oxide should be of suitable purity for direct marketing since the residue impurities known to be present in the original concentrates which may carry over into the iron oxide are of little significance in iron oxide intended for use in iron making. The principal residual elements such as zinc, lead, arsenic and antimony are expected to be of no consequence in iron making which would be the intended market for by-product iron oxide.

Wherever possible, equipment sizing, utility requirements, capital costs and labor requirements are based on published data for similar operations. Where published data are not available, capital costs were estimated by standard cost estimating procedures. Operating costs were estimated using the data presented in Table XVII. In general a conscious effort was made to be conservative in estimating both capital and operating costs. It was felt that this was necessary because of the lack of pilot and plant-scale data for some of the major operations. With additional data, it would probably be possible to reduce both capital and operating costs significantly.

TABLE XVII. Basis for Estimating Plant Operating Costs
(330 day per year operation)

1. Direct Labor (including fringe benefits)
    A. Operating - \$5.00/hr
    B. Maintenance - 3% of fixed capital costs
    C. Supervision - 10% of operating and maintenance labor
2. General Plant Overhead - 2/3 of direct labor
3. Utilities
    A. Power - \$0.01/kwh
    B. Natural Gas - \$0.75/1000 ft^3
    C. Cooling Water - \$0.03/1000 gal
    D. Process Water - \$0.20/1000 gal
    E. Boiler Water - \$0.75/1000 gal
    F. Steam - \$0.50/1000 pounds
4. Maintenance Supplies and Parts - 1.5% of fixed capital costs
5. Operating Supplies - 10% of direct labor
6. Pyrite - \$2/ton
7. Taxes and Insurance - 2% of plant cost
8. Depreciation - 15 year-straight line

NEUTRAL ROASTING SYSTEM

Storage and handling facilities would be required for the copper concentrate and the pyrite concentrate. Although drying may not be needed, it is included as a step in the process in order to minimize reactions which may increase the sulfur dioxide content of the neutral roasted flue gas. Drying of the concentrates would be accomplished in separate direct fired fluid bed driers. Each drier would be fired with natural gas. Maximum drier temperature would be 200°C. The off-gas from each drier would pass through a cyclone for particulate removal and then be vented to the stack. The dried concentrates would be fed to gas-fired fluid-bed roasters. The pyrite roaster would operate at 800°C. Residence time in the roaster would be 30 minutes. Two copper concentrate roasters would be used, each operating at 900°C. Residence time in the roasters would be one hour. The reactors would be fired with a rich fuel mixture to reduce the oxygen in the product gas. The off-gas and elemental sulfur from the roasters would pass through cyclones, for particulate removal, and then be combined. The combined gas stream would pass through a waste heat boiler, electrostatic precipitator and into a sulfur condenser. The liquid sulfur would be collected and granulated. A waste heat boiler for low pressure steam would be operated in conjunction with the sulfur condenser. The clean off-gas would be vented to the stack. The SO_2 in the off-gas would be approximately 1.5% of the sulfur in the combined feed. The neutral roasted products would pass from the roasters into a quench tank where they would be cooled and granulated (if necessary). Quenching could be in water.

Capital and operating costs for the neutral roasting operation are presented in Tables XVIII and XIX. Equipment, labor and utility requirements are based primarily on a paper published in 1968 by Mehta and Okane(28) entitled "Economies of Iron and Sulfur Recovery from Pyrite." In the estimates, allowances were made for inflation since 1968, higher operating temperatures of the roasters, and duplicate equipment requirements. Operating costs were calculated using the figures presented in Table XVII.

TABLE XVIII. Capital Cost for Neutral Roasting Operation

		Cost $1000's	
		Morenci	Pima
1.	Purchased Equipment Cost - Total*	$2,260	$2,160
2.	Equipment Installation (25% of Item #1)	565	540
3.	Piping Cost (20% of Item #1)	452	432
4.	Instrumentation (15% of Item #1)	339	324
5.	Electrical (10% of Item #1)	226	216
6.	Buildings (20% of Item #1)	452	432
7.	Site Preparation (10% of Item #1)	226	216
8.	Plant Design and Engineering (25% of Item #1)	565	540
9.	Auxiliaries (30% of Item #1)	678	648
	PLANT COST	$5,673	$5,508
10.	Contingency (15% of Plant Cost)	864	826
	TOTAL PLANT COST	$6,627	$6,334
11.	Plant Start-up Costs	125	125
12.	Interest During Construction (10%)	497	475
	TOTAL FIXED CAPITAL COST	$7,249	$6,934
13.	Working Capital (10% of fixed total cost)	725	693
	TOTAL CAPITAL COST	$7,974	$7,627

*Based on data from Mehta and O' Kane(28)

TABLE XIX. Operating Cost for Neutral Roasting Operation*

		Cost $1000's/yr	
		Morenci	Pima
1.	Operating Labor (6 men/shift)	$ 250	$ 250
2.	Maintenance Labor (3% of fixed capital costs)	217	208
3.	Supervision (18% of Items 1 & 2)	84	82
4.	General Plant Overhead (2/3 of Items 1-3)	367	360
5.	Power (6 kwh/ton feed)	30	30
6.	Natural Gas	1,460	1,400
7.	Boiler Feed Water	25	26
8.	Maintenance Supplies and Parts	109	104
9.	Operating Supplies	55	54
10.	Technical Services (lab, etc.)	35	35
11.	Pyrite ($2/ton)	90	246
12.	Taxes and Insurance (2% of plant cost)	132	127
	TOTAL	$2,854	$2,922
13.	Contingency (10% of Items 1-12)	285	296
14.	Depreciation (15 years)	532	508
	TOTAL OPERATING COST	$3,671	$3,726
	Cost Per Pound Copper Produced	$0.0185	$0.0188

*Based on data from Mehta and O'Kane(28)

Capital costs for Morenci and Pima concentrates were estimated to be \$7,974,000 and \$7,627,000, respectively. Yearly operating costs were \$3,671,000, and \$3,726,000, which is equivalent to \$0.0185 and \$0.0188 per pound of copper produced.

LEACHING OPERATION

In the leaching circuit the neutral roasted concentrates are reacted with hydrochloric acid in a series of closed leach tanks to produce H_2S and dissolve the iron. The leaching temperature is 80 to 85°C. The solids residence time in the leaching tanks is assumed to be three hours. Reaction temperatures are maintained using low pressure steam from the waste heat boilers. Mechanical agitation is provided in each leach tank. Liquid hold up in the leach tanks is about 200,000 gallons for the Morenci system and 130,000 gallons for the Pima system. The hydrogen sulfide produced would be scrubbed with dilute hydrochloric acid to remove any traces of hydrogen chloride, cooled to about 50°C and sent to the SO_2 recovery system (a portion of the H_2S would be consumed for copper recovery). A nitrogen or neutral flue gas sweep would be used on each leach tank to facilitate H_2S handling in the off-gas system. Nitrogen would be obtained from the oxygen plant (required for converter operation) and would amount to about one-half the H_2S on a volume basis.

The leach slurry would be filtered through a rotary drum filter. The washed solids would pass to the converter. The leach solution (plus wash) would flow to a copper recovery tank where it would be sparged with H_2S to precipitate any dissolved copper and precious metals. Liquid residence in the tank would be about 30 minutes. The resulting slurry would be filtered through a primary rotary drum filter and a polishing filter. The washed solids would be sent to the converter and the clear leach solution (plus wash) to the acid recovery system.

Estimating the capital and operating costs for the leaching operation is more subject to question than other sections of the process because the leaching operation has not been demonstrated on a pilot or plant scale.

TABLE XX. Capital Cost for the Leaching Operation

		Cost $1000's	
		Morenci	Pima
1.	Purchased Equipment Cost - Total	$ 2,700	$2,000
2.	Equipment Installation (25% of Item #1)	675	500
3.	Piping Cost (25% of Item #1)	675	500
4.	Instrumentation (15% of Item #1)	405	300
5.	Electrical (10% of Item #1	270	200
6.	Buildings (20% of Item #1)	540	400
7.	Site Preparation (10% of Item #1)	270	200
8.	Plant Design and Engineering (25% of Item #1)	675	500
9.	Auxiliaries (30% of Item #1)	810	600
	PLANT COST	$ 7,020	$5,200
10.	Contingency (20% of Plant Cost)	1,404	1,040
	TOTAL PLANT COST	$ 8,424	$6,240
11.	Plant Startup Cost	150	120
12.	Interest During Construction (10%)	632	468
	TOTAL FIXED CAPITAL COST	$ 9,206	$6,828
13.	Working Capital (10% of fixed capital cost)	921	683
	TOTAL CAPITAL COST	$10,127	$7,511

TABLE XXI. Operating Costs for the Leaching Operation

		Cost $1000's/yr	
		Morenci	Pima
1.	Operating Labor (5 men/shift)	208	208
2.	Maintenance Labor	276	205
3.	Supervision (18% of items 1 and 2)	87	74
4.	General Plant Overhead (2/3 of Items 1-3)	381	325
5.	Power	200	140
6.	Process Water	30	30
7.	Cooling Water	40	40
8.	Steam (available from waste heat boilers)	---	---
9.	Hydrochloric Acid (0.1% of inventory lost/day)	40	27
10.	Maintenance Supplies and Parts	138	102
11.	Operating Supplies	57	49
12.	Technical Services	100	100
13.	Taxes and Insurance	168	125
	TOTAL	$1,725	$1,425
14.	Contingency (15% of Items 1-12)	259	214
15.	Depreciation (15 years)	675	501
	TOTAL YEARLY OPERATING COST	$2,659	$2,140
	COST PER POUND OF COPPER PRODUCED	$0.0134	$0.0108

Equipment costs and labor requirements were estimated from data for various mineral leaching operations reported in the literature, allowing for inflation and a chloride-containing system. Capital and yearly operating costs for the Morenci and Pima systems are summarized in Tables XX and XXI. The capital costs are estimated to be $10,130,000 and $7,510,000 for the two cases. The lower capital cost for the Pima system results from the higher acid concentration used and the reduced volume of liquid which is handled. The yearly operating costs for the two cases are estimated to be $2,660,000 and $2,140,000, which corresponds to a cost $0.0134/lb of copper for the Morenci system and $0.0108/lb of copper for the Pima system.

ACID RECOVERY SYSTEM

In the acid recovery system the leach solution (plus wash) is treated to regenerate the hydrochloric acid and convert the ferrous chloride to ferric oxide. The system proposed for use is the Lurgi System,(4) which is used for the regeneration of hydrocloric acid pickle liquor. In the Lurgi-type system the leach solution is first concentrated in an evaporator. The concentrated liquor is then fed to a fluid bed reactor where the HCl and water are vaporized and the ferrous chloride converted to ferric oxide.

$$2FeCl_2 + 2H_2O + 1/2O_2 \longrightarrow 4HCl + Fe_2O_3$$

The reactor is operated at 800°C and is gas fired. The hot off-gas from the reactor passes through a cyclone to remove Fe_2O_3 particulates and then to the evaporator for heat recovery. The cooled gases from the evaporator pass to an absorber where the HCl is absorbed to form 4 to 5N hydrochloric acid, which is recycled to the leach circuit. The HCl free gases are then vented to the stack. The ferric oxide is obtained as chloride-free, free-flowing, coarse, granular solid having a bulk density of about 150 lb/ft^3.

Capital and operating costs for the acid recovery system are summarized in Tables XXII and XXIII. Operating costs were calculated using the data from Table XVI. Capital costs for the Morenci and Pima systems are estimated

TABLE XXII. Capital Costs for Acid Recovery System

		Cost $1000's	
		Morenci	Pima
1.	Purchased Equipment Cost - Total*	$ 4,100	$ 3,100
2.	Equipment Installation (25% of Item #1)	1,025	775
3.	Piping Cost (25% of Item #1)	1,025	775
4.	Instrumentation (15% of Item #1	615	465
5.	Electrical (10% of Item #1)	410	310
6.	Buildings (20% of Item #1)	820	620
7.	Site Preparation (10% of Item #1)	410	310
8.	Plant Design and Engineering (25% of Item #1)	1,025	775
9.	Auxiliaries (30% of Item #1)	1,230	930
	PLANT COST	$10,660	$ 8,060
10.	Contingency (15% of plant cost)	1,600	1,210
	TOTAL PLANT COST	$12,260	$ 9,270
11.	Plant Startup Costs	200	175
12.	Interest During Construction (10%)	920	695
	TOTAL FIXED CAPITAL COST	$13,380	$10,140
13.	Working Capital (10% of fixed capital cost)	134	101
	TOTAL CAPITAL COST	$13,514	$10,241

TABLE XXIII. Operating Costs for Acid Recovery System

		Cost $1000's/yr	
		Morenci	Pima
1.	Operating Labor	210	210
2.	Maintenance Labor (3% of fixed capital costs)	401	304
3.	Supervision (18% of Items 1 and 2)	110	93
4.	General Plant Overhead (2/3 of Items 1-3)	483	405
5.	Power	50	35
6.	Natural Gas	4,950	3,300
7.	Cooling Water	60	40
8.	Process Water	100	65
9.	Hydrochloric Acid (22° Be')	80	60
10.	Maintenance Supplies and Parts	200	152
11.	Operating Supplies	72	61
12.	Technical Services	40	40
13.	Taxes and Insurance	245	185
	TOTAL	$7,001	$4,950
14.	Contingency (10% of Items 1-13)	700	495
15.	Depreciation	901	683
	TOTAL OPERATING COST	$8,602	$6,128
	COST PER POUND COPPER PRODUCED	$0.0434	$0.0309

to be \$13,500,000 and \$10,200,000, respectively. The yearly operating costs are estimated at \$8,600,000 and \$6,100,000, corresponding to \$0.043 and \$0.031 per pound of blister copper produced.

Acid recovery systems of the size required to treat the plant leach liquor have not been built to date. There is, therefore, some question as to scale-up from existing units. In addition, there is only limited operating data available on the Lurgi system. For these reasons, conservative estimates were used for both capital costs and operating costs. By a more detailed study of the Lurgi and other systems such as that of Haveg,(4) it should be possible to reduce both capital and operating costs significantly.

Natural gas for heating the reactors and evaporators accounts for more than 60% of the yearly operating costs. By improved design, additional heat recovery (multiple effect evaporators) etc., it should be possible to reduce fuel requirements by a significant amount.

SO_2 RECOVERY SYSTEM

The citrate process developed by the U.S. Bureau of Mines for recovery of SO_2 involves the reaction of SO_2 and H_2S in an aqueous solution to form elemental sulfur.(34)

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

The basic steps in the process are:

1. Washing of the cooled SO_2-bearing gas to remove particulates and SO_3,
2. absorption of the SO_2 from the cleaned gas by a solution of citric acid, sodium citrate and sodium thiosulfate,
3. reaction of the absorbed SO_2 with H_2S in a closed vessel, precipitating elemental sulfur and regenerating the absorption solution, and
4. recovery of the sulfur by oil melting.

SO_2 recoveries of 90 to 99% have been reported.(36) In this study a recovery of 98% was assumed. A small amount of the SO_2 is converted to sulfate in the process. For this study it was assumed that enough H_2S would be required to react with all of the SO_2 absorbed, ignoring any possible sulfate formation.

The citrate process has only been demonstrated on a small pilot-plant scale. Scale up to the size required for this study may be questionable until the plant scale operation, which is underway at the Bunker Hill Smelter, Kellogg, Idaho, has been demonstrated. If a lower SO_2 recovery could be tolerated (90 to 95%) then a modified Claus process might be used. The Claus process has been demonstrated in large-scale applications and would have lower capital and operating costs than the citrate process.

Capital and operating costs for SO_2 recovery using the citrate process were estimated using Bureau of Mines data reported in 1973(36) with an allowance for inflation. It was assumed that the gas flow to the SO_2 recovery unit would be approximately 30,000 SCFM with an average SO_2 concentration of about 6%. To account for fluctuations in gas flow the system was sized to handle 38,000 CFM. Capital and yearly operation costs for each case under consideration are summarized in Tables XXIV and XXV. Estimated capital costs for the Morenci and Pima systems are $8,270,000 and $8,620,000, respectively, while yearly operating costs are estimated to be $2,100,000 and $2,180,000. The corresponding costs per pound of copper produced are $0.0106 and $0.0110.

CONVERTER OPERATION

The copper-bearing solids from the leach circuit are fed directly to a converter. This feed material is high in copper (∿50 wt%) and low in iron (≤10 wt% Fe). The sulfur content (∿20 wt%) is also lower than in the normal converter feed. For this reason, much of the heat required for converted operation must be supplied by natural gas or other fuel. A portion of the oxygen required for reaction with the sulfur and burning of the natural gas will be supplied from an oxygen plant (∿20%). The rest will be supplied by air. The off-gas from the converter will pass through a waste heat boiler and then through cleaning equipment to remove the bulk of the particulates and cool the gas to about 300°C. The gases then pass to the SO_2 recovery unit.

TABLE XXIV. Capital Costs for SO_2 Recovery System*

		Cost $1000's	
		Morenci	Pima
1.	Purchased Equipment Cost - Total	$2,300	$2,400
2.	Equipment Installation (25% of Item #1)	575	600
3.	Piping Cost (25% of Item #1)	575	600
4.	Instrumentation (15% of Item #1)	345	360
5.	Electrical (10% of Item #1)	230	240
6.	Buildings (20% of Item #1)	460	480
7.	Site Preparation (10% of Item #1)	230	240
8.	Plant Design and Engineering (25% of Item #1)	575	600
9.	Auxiliaries (30% of Item #1)	690	720
	PLANT COST	$5,980	$6,240
10.	Contingency (15% of plant cost)	897	936
	TOTAL PLANT COST	$6,877	$7,176
11.	Plant Startup Costs	125	125
12.	Interest During Construction (10%)	516	538
	TOTAL FIXED CAPITAL COST	$7,518	$7,839
13.	Working Capital (10% of fixed capital cost)	752	784
	TOTAL CAPITAL COST	$8,270	$8,623

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*Based on data from J. B. Rosenbaum, et. al.(36)

TABLE XXV. Operating Costs for SO_2 Recovery System

		Cost $1000's/yr	
		Morenci	Pima
1.	Operating Labor (4 men/shift)	$ 167	$ 167
2.	Maintenance Labor	226	235
3.	Supervision (18% of Items 1 and 2)	71	73
4.	General Plant Overhead (2/3 of Items 1-3)	309	317
5.	Power	20	21
6.	Natural Gas	50	52
7.	Steam (waste steam available at no charge)	---	---
8.	Process Water	15	16
9.	Cooling Water	35	36
10.	Chemicals	162	169
11.	Maintenance Supplies and Parts	113	118
12.	Operating Supplies	46	46
13.	Technical Services	60	60
14.	Taxes and Insurance	138	144
	TOTAL	$1,412	$1,454
15.	Contingency (10% of Items 1-14)	141	145
16.	Depreciation (15 year)	551	575
	TOTAL OPERATING COST	$2,104	$2,176
	COST PER POUND COPPER PRODUCED	$0.0106	$0.0110

The copper leaves the converter at a purity of about 98.8% and contains about 0.2% sulfur. The blister copper is transferred to a holding furnace and then to a refining furnace. The copper from the refining furnace is cast into anodes for further refining. The off-gases from the holding and refining furnaces are vented to the stack. Approximately 0.1% of the sulfur in the original concentrates would be present in the off-gas as SO_2. The cost estimates include all operations through the casting of anodes but does not include subsequent operations.

The slag from the converter contains a small but significant amount of copper. This slag would be recycled into the concentrator-flotation plant where the copper would be recovered as part of the copper concentrate.

The steam produced in the waste heat boiler meets most of the steam requirements of the entire plant operation. Additional steam capacity required is minimal.

The capital and operating costs for the converter operation are summarized in Tables XXVI and XXVII. Equipment and operating cost data were obtained from a 1973 Bureau of Mines publication by Bennett, et al.(38) Capital costs for the Morenci and Pima systems are $12,200,000 and $12,700,000, respectively. Yearly operating costs are estimated to be $6,120,000 and $6,260,000, which is equivalent to $0.0309 and $0.0316 per pound of anode copper.

TOTAL PROCESSING COSTS

The total estimated capital and yearly operating costs for a 300 ton/day copper smelter are summarized in Tables XXVIII and XXIX. The capital costs for the Morenci and Pima cases are $52,000,000 and $46,700,000, respectively. These estimates include all of the facilities required to convert copper concentrate into copper anodes.

The yearly operating costs for the two cases are estimated at $23,150,000 and $20,430,000, which corresponds to a cost of $0.117 per pound of anode copper for the Morenci case and $0.103 for the Pima case.

TABLE XXVI. Capital Costs for Converter Operation

	Cost $1000's	
	Morenci	Pima
1. Purchased Equipment Cost - Total*	$ 3,400	$ 3,500
2. Equipment Installation (25% of Item #1)	850	875
3. Piping Cost (20% of Item #1)	680	700
4. Instrumentation (15% of Item #1)	510	525
5. Electrical (10% of Item #1)	340	350
6. Buildings (25% of Item #1)	850	875
7. Site Preparation (10% of Item #1)	340	350
8. Plant Design and Engineering (25% of Item #1)	850	875
9. Auxiliaries (30% of Item #1)	1,020	1,050
PLANT COST	$ 8,840	$ 9,100
10. Contingency (15% of plant cost)	1,326	1,365
TOTAL PLANT COST	$10,166	$10,465
11. Plant Startup Costs	175	175
12. Interest During Construction (10%)	762	785
TOTAL FIXED CAPITAL COST	$11,103	$11,425
13. Working Capital (10% of fixed capital cost)	1,110	1,143
TOTAL CAPITAL COST	$12,213	$12,668

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*Based on data from Bennett, et.al.(38)

TABLE XXVII. Operating Costs for Converter Operation*

		Cost $1000's/yr	
		Morenci	Pima
1.	Operating Labor (28 men/shift)	$1,165	$1,165
2.	Maintenance Labor	340	345
3.	Supervision (18% of Items 1 and 2)	271	272
4.	General Plant Overhead (2/3 of Items 1-3)	1,184	1,188
5.	Power	160	162
6.	Natural Gas	750	755
7.	Cooling Water	30	30
8.	Boiler Water	30	30
9.	Flux-Converter ($5.50/ton)	91	163
10.	Refractory	150	150
11.	Maintenance Supplies and Parts	167	171
12.	Operating Supplies	178	178
13.	Technical Services	100	100
14.	Taxes and Insurance	203	209
	TOTAL	$4,819	$4,918
15.	Contingency (10% of Items 1-14)	482	492
16.	Depreciation (15 years)	814	845
	TOTAL YEARLY OPERATING COSTS	$6,115	$6,255
	COST PER POUND OF COPPER ANODE	$0.0309	$0.0316

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*Based on data from Bennett, et. al.(38)

TABLE XXVIII. Capital Costs for a 300 Ton/Day Copper Smelter

		Cost $1000's	
		Morenci	Pima
1.	Neutral Roasting Operation	$ 7,974	$ 7,627
2.	Leaching Operation	10,127	7,511
3.	Acid Recovery System	13,514	10,241
4.	SO_2 Recovery Unit	8,270	8,623
5.	Converter Operation	12,213	12,668
	TOTAL	$52,098	$46,670

TABLE XXIX. Yearly Operating Costs for a 300 Ton/Day Copper Smelter

		Cost $1000's/yr	
		Morenci	Pima
1.	Neutral Roasting Operation	$ 3,671	$ 3,726
2.	Leaching Operation	2,659	2,140
3.	Acid Recovery System	8,602	6,128
4.	SO_2 Recovery Unit	2,104	2,176
5.	Converter Operation	6,115	6,255
	TOTAL OPERATING COSTS	$23,151	$20,425
	COST PER POUND OF ANODE COPPER	$0.117	$0.103
6.	Credit for Sulfur ($20/ton)	3,461	3,185
7.	Credit for Fe_2O_3 ($10/ton)	1,757	1,776
	COST PER POUND OF ANODE COPPER (with credit for S and Fe_2O_3)	$0.091	$0.078

If credit is allowed for the sulfur ($20/ton) and ferric oxide ($10/ton), the operating costs are reduced to $0.091 and $0.078 for the Morenci and Pima cases, respectively.

Although for comparison it would be most convenient to have an operating, elemental sulfur-producing, state-of-the-art SO_2 air pollution abatement system integrated with a conventional copper smelter, such a combination does not, to our knowledge, exist at this time. The extensive study made by the Fluor Utah Corporation and as authoritatively reviewed by Swan(39,40) is therefore taken as the basis for reference for this comparison. From that study which covers the entire U.S. copper smelting industry, the installation cost for 90% emissions control for an add-on system resulting in elemental sulfur production would amount to $415,000,000 (1970 costs). The annual operating cost for these additional facilities without credit for by-product sulfur was reported to be $130,000,000, which would amount to an additional cost for the production of copper of 4-1/3 cents per pound, based on this 1970 study estimate. A reasonable addition to this cost of 1 to 1.5 cents per pound should be added to account for inflationary factors since the 1970 estimate was made. It is likely then that at present and near-future costs the addition should be in the range of 5 to 6 cents per pound of copper for emissions control as provided for in the Fluor study. A similar situation should be projected for overall smelting costs. A 1973 U.S. Bureau of Mines report(38) estimated the overall smelting cost to be 6.4 cents per pound of copper. With anticipated near-future increases in fuel and labor costs, this figure should probably also be adjusted upward to a range of 7 to 8 cents. Thus, by combining these cost figures, a figure of 12 to 14 cents is obtained for present and near-future costs for copper smelting with equivalent sulfur dioxide air pollution abatement including recovery of some portion of the sulfur in elemental form. This range can be compared with the 10 to 12 cents range for the proposed process concept with a tendency to favor the lower figure. These results indicate that the proposed process concept has a favorable economic outlook when viewed under circumstances which appear to be conservative.

CONCLUSIONS

ADEQUATE PRODUCTION OF HYDROGEN SULFIDE FOR ELEMENTAL SULFUR RECOVERY IS ACHIEVABLE WITHOUT NEED FOR ANY SPECIFIC CHEMICAL REDUCTANT

The proposed process concept can result in the production of sufficient hydrogen sulfide from pyritic copper concentrates for reaction with sulfur dioxide emissions from converters for elemental sulfur recovery without need for any specific chemical reductant. The process may be able to use any type of fuel.

THE ECONOMICS OF AN OVERALL SMELTING PROCESS UTILIZING THE PROCESS APPEARS FAVORABLE

The preliminary economic assessment indicates that an overall smelting process employing the concept has favorable costs for achieving copper production with adequate sulfur emissions control. Credit for the iron oxide and elemental sulfur provide an even more favorable economic picture at conservative values. These preliminary evaluations suggest an adequate basis for continued support on the development of the process through the pilot plant design phase by EPA and industry.

NEUTRAL ROASTING IS A FEASIBLE MEANS OF CONVERTING THE IRON SULFIDE TO THE ACID-SOLUBLE FORM

The results of this study show that neutral roasting is a chemically feasible means of assuring the maximum selective solubilization of the iron sulfide in pyritic copper concentrates without major dissolution of copper. Neutral-roasting as studied by others for pyrite alone supports the proposed process as a feasible and practical method for also treating the pyritic copper concentrates for preliminary removal of a significant fraction of the sulfur initially as elemental sulfur as well as for converting the remaining iron sulfide into a soluble form.

HYDROCHLORIC ACID LEACHING IS A PRACTICAL METHOD FOR HYDROGEN SULFIDE PRODUCTION

Hydrochloric acid leaching of neutral-roasted concentrates is a direct and practical means for selective dissolution of iron and release of hydrogen sulfide. Copper, which may be dissolved in minor amounts, is recoverable to a major extent along with any solubilized precious metals (silver) by simple treatment of the cooled solution with the hydrogen sulfide. Hydrogen sulfide can be produced by this means in amounts sufficient for reaction with all of the sulfur dioxide released in the step of converting the enriched copper sulfide to blister copper. Known present state-of-the-art technology is applicable to conduct the hydrogen sulfide-sulfur dioxide reaction for high-purity elemental sulfur production via the so-called Claus process or by the U.S. Bureau of Mines Citrate process.

HYDROCHLORIC ACID REGENERATION IS A PRESENT STATE-OF-THE-ART PROCESS

Hydrochloric acid regeneration from acid-ferrous chloride solutions is regarded as a present state-of-the-art process which does not need demonstration at the laboratory scale. Existing processes which are already employed on a large scale in the steel pickling industry can accommodate ferrous chloride solutions of any concentration and acidity.

THE BLISTER COPPER WILL BE RECOVERED IN SATISFACTORY YIELD AND QUALITY

The process is essentially a closed one insofar as copper processing is concerned. Solids are processed by present state-of-the-art methods in conventional converters, liquids are specially treated for very effective copper recovery. Dusts would be retained by the usual methods. If anything, a higher yield of copper would be anticipated because of the avoidance of the usual reverberatory slag losses. Quality should be essentially no different from the usual blister copper. The small amounts of converter slag would be recycled to the concentrator for additional copper recovery. In conventional smelting this slag is added instead to the reverberatory furnaces.

THE IRON OXIDE AND HYDROGEN SULFIDE DERIVED SULFUR WILL BE OF HIGH QUALITY

The iron oxide by-product produced during hydrochloric acid regeneration from ferrous chloride solutions is expected to be of high quality and suitable for marketing for steel-making. Small amounts of other metal chlorides which may also be oxidized, such as zinc, principally, and possibly lead, are expected to be of no consequence in determining the suitability of the iron oxide. The sulfur obtained via the hydrogen sulfide-sulfur dioxide is expected to be of the very high purity as represented by that typically produced via the Claus process. The sulfur produced in the neutral roasting operation will be relatively impure but can be purified to suitable quality by present state-of-the-art processes.(26)

SIGNIFICANT ECONOMIES APPEAR TO BE LIKELY FOR THE PROCESS

Although it is felt that the preliminary economic evaluation of the process concept is adequate to encourage continued consideration and support for development of an overall process, significant economies appear to be probable by more intensive consideration of alternative lower-cost fuels and engineering refinements to assure increased heat economy. The estimates, for convenience and simplicity at this stage of the investigation, assumed the use of high-cost natural gas as the fuel.

THE PROPOSED PROCESS IS APPLICABLE IN ANY SULFIDE SMELTER HAVING SUFFICIENT PYRITE

Given a sufficient supply of pyrite, any operator of a conventional smelter for copper sulfides concentrates could consider the installation of the proposed process. Such installation may be more readily incorporated into a new smelter than in an old one. Space and physical arrangement would be the principal problems in modifying old smelters to accommodate the revised process.

INCREASED COPPER AND PRECIOUS METAL RECOVERY FROM THE ORE BODY SHOULD BE POSSIBLE

By use of large amounts of pyrite which is normally discarded, the small but significant amounts of copper and accompanying precious metals in such discard would now be almost completely recovered at essentially very low incremental cost. For exploitation of some ore bodies the increased recoveries may be quite significant.

OTHER BENEFITS IN RECOVERY OF METAL VALUES, RESOURCE CONSERVATION AND ECONOMICS MAY BE REALIZED

Because of the need for pyrite, a lower-grade ore may be beneficially utilized. The use of the major slag-forming minerals such as silica and limestone would be greatly reduced. The handling and disposal of the large amounts of useless slag would be greatly reduced. The two other major components of the concentrates, iron and sulfur, would be recovered in suitable purity such that beneficial utilization could then be anticipated with significant economic credit to the overall process. The large-volume, low-strength sulfur dioxide flue gases characteristic of reverberatory furnace operations would be avoided.

RECOMMENDATIONS

In view of the demonstrated chemical feasibility, favorable economics and indicated other significant benefits which appear to be probable by the operation of the proposed process concept, the following recommendations in support of continued development of the integrated process appear appropriate:

1. Large bench-scale experimental work should be continued to obtain needed data on dynamic systems suitable for the design of a pilot plant. Such work would be done on the steps of neutral roasting, hydrochloric acid leaching, residual copper precipitation and separation of solid, enriched copper sulfide and residues from the ferrous chloride leach liquors.
2. Work jointly with an appropriate architect-engineer-constructor to assure that information suitable for the design and estimating of the acid regeneration system is obtained in the continued laboratory studies.
3. Conduct engineering studies to determine the most economical fuel to be used and equipment refinements which may be justified to assure most beneficial heat economy.
4. Refine the economic assessment of the overall process.
5. Conduct process engineering and economic comparisons between this process and other copper smelting processes which exist in the U.S. or are being considered for the production of elemental sulfur.

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